Point-by-Point Response

Reviewer: 1

General comments: *This paper presents the comparison of three different chemical mechanisms (CB06, SAPRC07, RACM2)f embedded in the CMAQ model frame focusing on ozone and its precursors. Model results are compared to trace gas and radical measurements conducted at an urban and a suburban site in Chengdu, China. Eventually, a budget analysis of ozone and ROx radicals and a sensitivity analysis of ozone to NOx and VOC emissions is presented.*

Trends found in the ozone production and loss pathways are not unexpected. Differences in the chemical mechanisms arise mainly from variations in radical concentrations and mechanism-specific reaction pathways, which however are not discussed in detail.

Overall, this paper showcases the impact of using different chemical mechanisms in modelling air quality in China. Previous studies already investigated the intercomparibility of the different chemical mechanisms in different regions, however, to the reviewer's knowledge there is no study in the Chengdu region yet. Even though, the presented data set is comparably small, it complements the previous studies and gives insights into the sensitivity of air quality modelling in China to the chosen chemical mechanism.

Therefore, the reviewer recommends this paper to be considered for publication after major changes have been made.

Reply: Thank you very much for your careful review and valuable comments. We have tried our best to revise the manuscript according to your comments. The corrections in the manuscript are marked in blue.

Major comments

1. **Comments:** *In the introduction, the atmospheric photochemistry is extensively described which rather fits in Section 2.4. A schematic of the NOx and ROx radical cycle may help the reader to follow more easily. In addition, the description can be shortened, as currently it rather reads like a textbook. It is striking that RO2 isomerisation was not mentioned at all. Since the paper is focused on photochemistry it should be stressed that ozone is mainly formed from the oxidation of VOCs by OH. In line 62 for example, it should be made clear that the OH oxidation of VOCs is an important source of primary ROx radicals, with OH being formed through the photolysis of O3 and HONO. Later in Section 3.3.2, the H2O2/HNO3 ratio is mentioned as a measure for the chemical regime which should be introduced in Section 2.4 as well.*

Reply: Thank you for your suggestion.

(1) We agree that the original Introduction contained an overly extensive description of atmospheric photochemistry and the description of the NO_x and RO_x radical cycle should be shortened. In the revised manuscript, we have condensed this part and minimized textbook definition as much as possible.

"Although tropospheric O_3 is generated by NO_2 photolysis (Dickerson et al., 1982), its net production

of O_3 was governed by the coupling between the NO_x cycle and RO_x cycle, where RO_x denotes the sum of hydroxyl radicals (OH), hydroperoxyl radicals (HO_2), and organic peroxy radicals (RO_2) (Tan et al., 2019; Wang et al., 2017). Representative reactions involved in these coupled cycles are summarized in Table S1 and a simplified schematic O_3 formation mechanism and coupling of NO_x cycle and RO_x cycle was shown as Fig. S1. Due to this coupled NO_x-RO_x cycle involves highly nonlinear photochemical reactions, accurately simulating O_3 formation remains challenging." Line 50-56

Moreover, we also have supplemented a schematic of the NO_x and RO_x radical cycle (Figure S1) and a table that provides the description of representative reactions for NO_x and RO_x radical cycle (Table S1) for better understanding these processes.

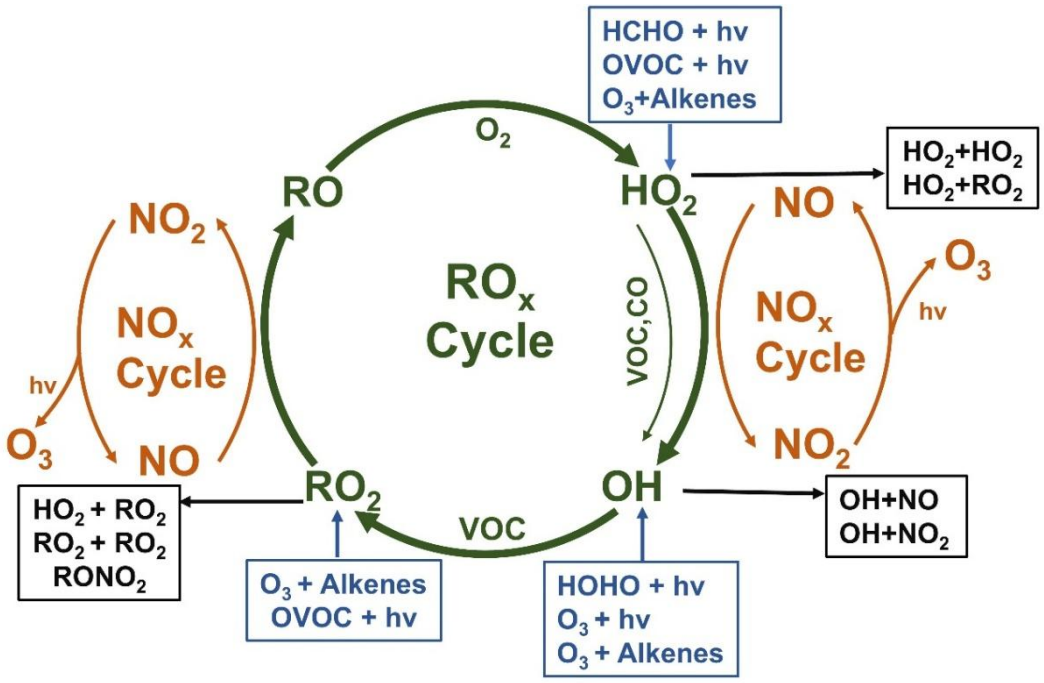


Figure S1 Schematic of simplified ozone formation mechanism and the coupling of the NO_x and RO_x radical cycle. The primary source reactions and the termination reactions of RO_x radicals were shown in blue and black, respectively.

Table S1 The representative reactions involved in NO_2 photolysis and initiation, chain propagation, and termination of RO_x radical cycle for ozone formation.

Reactions	**No.**
$NO_2 + hv\ (< 424\ nm) \rightarrow O(^3P) + M$	(R1)
$O(^3P) + O_2 + M \rightarrow O_3 + M$	(R2)
$O_3 + NO \rightarrow NO_2 + O_2$	(R3)
Initiation reactions of the RO_x cycle	
$O_3 + hv\ (<\ 340\ nm) \rightarrow O(^1D) + O_2$ $O(^1D) + H_2O \rightarrow OH + OH$	(R4)
$HONO + hv\ (<\ 400\ nm) \rightarrow OH + NO$	(R5)
$HCHO + hv\ (<\ 335\ nm) + 2O_2 \rightarrow HO_2\ +\ CO$	(R6)

$Alkenes + O_3 \rightarrow OH, HO_2, RO_2 + products$	(R7)
Chain propagation reactions of the RO_x cycle	
$OH + Hydrocarbons + O_2 \rightarrow RO_2 + H_2O$	(R8)
$HCHO + OH + O_2 \rightarrow CO + H_2O + HO_2$	(R9)
$CO + OH + O_2 \rightarrow CO_2 + HO_2$	(R10)
$RO_2 + NO \rightarrow RO + NO_2$ $RO + O_2 \rightarrow RCHO + HO_2$	(R11)
$HO_2 + NO \rightarrow OH + NO_2$	(R12)
$HO_2 + O_3 \rightarrow OH + 2O_2$	(R13)
Termination reactions of the RO_x cycle	
$OH + NO_2 \rightarrow HNO_3$	(R14)
$OH + NO \rightarrow HONO$	(R15)
$RO_2 + NO \rightarrow RONO_2$	(R16)
$RO_2 + RO_2 \rightarrow products$	(R17)
$RO_2 + HO_2 \rightarrow ROOH + O_2$	(R18)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(R19)
$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2$	(R20)

Note. The reactions highlighted in orange are related to NO_x cycle.

In addition, we have moved the detailed description of the atmospheric photochemistry to the Section 2.4 and Section 2.5. Section 2.4 describes the calculation of the ozone budget. Section 2.5 has been added for describing the diagnostic analysis of the RO_x budget to facilitate the reader's understanding of the RO_x budget.

(2) We also agree that RO_2 isomerisation is an important pathway in atmospheric RO_2 chemistry, such as RO_2 isomerization is one of OH source(Peeters et al., 2009). Given that RO_2 isomerization-mediated OH recycling is pronounced solely in low-NO environments (e.g., forests), whereas the urban and suburban settings investigated here are typified by high NO_x concentrations, the RO_2 + NO reaction overwhelmingly outcompetes the intramolecular hydrogen-shift pathway. Moreover, in this study, we mainly focus on the ozone formation and the reaction-rate for ozone formation is quantified through calculating the conversion of NO to NO_2 by HO_2 and RO_2 radicals, as represented by Equation (1). For this specific diagnostic, the key quantity is the total oxidation rate of NO to NO_2 by HO_2 and RO_2 radicals, and it is not necessary to separate whether a given RO_2 radical is produced directly from VOC oxidation or through subsequent RO_2 isomerisation pathways. Consequently, the RO_2 isomerization is not mentioned in this study.

(3) We clarified that the formation of ozone cannot be interpreted mainly from the oxidation of VOCs by OH radical. The O_3 formation is indirectly from the conversion of NO to NO_2 through RO_2 and HO_2 radical, followed by NO_2 photolysis. This mechanism had been described in the original manuscript in the discussion of the RO_x-NO_x cycles. For example, "in the real atmosphere, other key oxidizing agents such as hydroperoxyl radical (HO_2) and organic peroxyl radical (RO_2) radicals in the

troposphere can also oxidize NO to NO_2 (e.g., R4–R5). These reactions compete with R3, reducing the consumption of O_3 through reaction with NO and thus leading to O_3 accumulation (Wang et al., 2017). Under the action of the "NO_x cycle" formed by R2, R4, and R5, O_3 is efficiently generated without the consumption of NO_x." (Line 49-53), and "As discussed above, photochemically produced O_3 is a secondary pollutant formed from its precursors through a series of highly nonlinear photochemical reactions (e.g., the ROx and NOx cycles)." (Line 94-95). Combined with the updated description of the ozone formation mechanism in the revised manuscript, as well as Table S1 and Figure S1, we believe this will better help reader understand the ozone formation mechanism.

(4) Following the RO_x budget framework of previous studies(Xue et al., 2016; Wang et al., 2017; Tan et al., 2019), the reactions of OH oxidation of VOC is a secondary source of RO_2 radical and is not treated as a primary source of total RO_x radicals, for this reaction consumes OH radical while producing RO_2 radical (shown as R9 in the manuscript and R8-9 Table S1 in the revised manuscript). It represents the RO_x radical chain propagation in the RO_x cycle, rather than a source of primary RO_x production outside the RO_x cycle. Therefore, in line 62 of the original manuscript, OH oxidation of VOC was not described as a source of primary RO_x radicals.

(5) In the supplemented Section 2.5, we have added an explicit introduction to the H_2O_2/HNO_3 ratio as a diagnostic indicator of photochemical regimes.

"Under high NO_x conditions, the terminations of the RO_x and NO_x cycles are primarily controlled by OH + NO_2 and the organic-nitrate-forming branch of RO_2 + NO, which sequester reactive nitrogen as HNO_3 and $RONO_2$, respectively. In contrast, under low NO conditions, the terminations of RO_x cycle were mainly driven by the self-reaction of HO_2, and cross-reactions between HO_2 and RO_2, which further produce hydrogen peroxide (H_2O_2) and organic hydroperoxides (ROOH). Therefore, the ratios of major products or its production rates from termination reactions, such as H_2O_2/HNO_3, can provide a useful indicator of the prevailing radical-termination regime and the associated NO_x chemical environment. Previous studies examined that the H_2O_2/HNO_3 can be used as a robust indicator for determining O_3 formation regimes (Wei et al., 2018; Liu et al., 2010; Cordiner et al., 2002). The classic threshold of H_2O_2/HNO_3 separating the O_3 formation regimes threshold range is [0.35, 0.65], whereas the threshold also varies with the region and season (Li et al., 2011; Wei et al., 2018; Xing et al., 2019)." Line 269-280

2. **Comments:** *In the conclusions, the overall comparison with results from previous studies, mentioned in the introduction, is missing. How does Chengdu compare with, e.g. Japan. There are more studies about the comparison of different chemical mechanisms in CMAQ, e.g.: Shareef et al. (Appl. Sci. 12, 8576 (2022)), Gupta and Mohan (Atmos. Env. 122, 220-229 (2015)).*

Reply: Thank you for your suggestion.

(1) We have added discussions of previous studies, suggested by the reviewer, that compared different chemical mechanisms in CMAQ. Specifically, we have cited *Shareef et al. (Appl. Sci. 12, 8576 (2022)),*

and Gupta and Mohan (Atmos. Env. 122, 220-229 (2015)), alongside other relevant studies that have evaluated mechanism-dependent ozone simulations in various geographical contexts. This addition establishes a broader literature foundation and clarifies the research gap that our study aims to fill.

"CBMZ produced less O_3 overestimation than RACM in WRF/Chem simulations over Delhi (Gupta and Mohan, 2015)." Line 109-110
"Similarly, SAPRC07 and RACM2 yielded higher summer O_3 than CB6R3 in Alberta, accompanied by OH increases of about 30% and 100%, respectively (Shareef et al., 2022)." Line 112-113

(2) In the Conclusions Section, we have expanded the discussion to include a comparison between our simulation results over Chengdu and those reported in previous mechanism-comparison studies conducted in other regions.

"SAPRC07 and RACM2 simulated higher and comparable O3 concentrations (94.8-96.1 ppbv, MDA8) than CB06 (~80 ppbv, MDA8). This result is broadly consistent with previous mechanism intercomparisons (Kitayama et al., 2019; Shareef et al., 2022), which also reported that RACM2 and SAPRC07 yield similar O_3 concentrations, while carbon bond mechanisms produce lower values, with inter mechanism differences reaching up to 10 ppb over Japan (Kitayama et al., 2019)." Line 699-703

3. **Comments:** *Overall, the impact of the different mapping strategies for the different chemical mechanisms on the results is not clear to the reader. Fig. 9 indirectly shows the different VOC distribution. Would it make sense to show this comparison in the beginning?*
Reply: Thank you for your suggestion.
(1) Regarding the influence of mapping strategies, we carefully considered this issue in the simulation design. First, all emissions were based on the same version of the MEIC inventory and MEGAN, ensuring consistency in the emission source strengths. Second, for explicit VOC species shared by different chemical mechanisms, such as benzene, ethene, isoprene, and glyoxal, we checked the emission totals in the inventory item by item and ensured that they were identical across mechanism simulations. This eliminates emission-related uncertainty for these explicit species. Third, for lumped VOC species, we applied consistent mapping principles as far as possible, based on criteria such as carbon-bond structure, reactivity, and functional groups, so that the mapping rules remained comparable among mechanisms. Nevertheless, since the methods of different chemical mechanisms lumping VOC species is inconsistent, some differences in the mapping VOC speciates are unavoidable. This uncertainty originates from the theoretical species-definition framework of each mechanism and cannot be completely removed during emission preprocessing. However, by applying the unified mapping principles described above, we minimized its influence on the comparability of the results.
In addition, Fig. 9 also indirectly supports the reasonableness of the emission-mapping strategies used in this study, for that the reaction rates of OH with the major primary-emission VOC categories are generally similar among the three mechanisms. Although the OH reaction rate with alkanes is slightly higher in the CB06 mechanism than in the other two mechanisms, this mainly results from the mapping

of more species into the PAR category, which represents carbon-carbon single bonds in CB06. Since alkanes are relatively less reactive, a higher OH reaction rate with alkanes does not necessarily imply a substantial effect on O_3 simulation. Therefore, we consider that the mapping strategies do not materially affect the key conclusions of this study. In addition, to provide a clearer description of the emission mapping process for different photochemical mechanisms, we have split the original Table S5 into Tables S5-S7, which present the categories of emission species for each photochemical mechanism in the CMAQ.

Table S5 The anthropogenic VOC emission species input into the CB06 mechanism in the CMAQ model.

Mechanism	Category	Model Species	Definition
CB06	Alkanes	ETHA	ethane
		PRPA	propane
		PAR	carbon-carbon single bond
	Alkenes	ETH	ethene (ethylene)
		OLE	terminal alkene bond
		IOLE	internal alkene bond
		ISOP	isoprene
		TERP	monoterpenes
	Aromatics	BENZENE	benzene
		TOL	toluene and other monoalkyl aromatics
		XYLMN	xylene and other polyalkyl aromatics except naphthalene
		CRES	cresol and higher molecular weight phenols
	Aldehydes	FORM	formaldehyde
		ALD2	acetaldehyde
		ALDX	aldehydes with 3 or more carbons
		GLY	glyoxal
		MGLY	methyl glyoxal
	Acids	FACD	formic acid
		AACD	acetic acid
	Others	ETHY	ethyne (acetylene)
		ACET	acetone
		ISPD	isoprene reaction products (methacrolein, methylvinyl ketone, others)
		MEOH	methanol
		ETOH	ethanol
		KET	carbon-ketone bond

Table S6 The anthropogenic VOC emission species input into the SAPRC07 mechanism in the CMAQ model.

Mechanism	Category	Model Species	Definition
SAPRC07	Alkanes	ALK1	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 2 and 5 × 10^2 ppm^{-1} min^{-1}. (Primarily ethane)
		ALK2	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 5 × 10^2 and 2.5 × 10^3 ppm^{-1} min^{-1}. (Primarily propane and acetylene)
		ALK3	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 2.5 × 10^3 and 5 × 10^3 ppm^{-1} min^{-1}.
		ALK4	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 5 × 10^3 and 1 × 10^4 ppm^{-1} min^{-1}.

	ALK5	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} greater than 1×10^4 ppm^{-1} min^{-1}.
Alkenes	ETHE	Ethene
	OLE1	alkenes (other than ethene) with $k_{OH} < 7 \times 10^4$ ppm^{-1} min^{-1}.
	OLE2	Alkenes with $k_{OH} > 7 \times 10^4$ ppm^{-1} min^{-1}.
	ISOP	isoprene
	TERP	terpenes
Aromatics	ARO1	aromatics with $k_{OH} < 2 \times 10^4$ ppm^{-1} min^{-1}.
	ARO2MN	ARO2 minus naphthalene
	BENZENE	benzene
	CRES	phenols and cresols
Aldehydes	HCHO	formaldehyde
	CCHO	acetaldehyde
	RCHO	lumped C3+ aldehydes (mechanism based on propionaldehyde)
	BALD	aromatic aldehydes (e.g., benzaldehyde)
	GLY	glyoxal
	MGLY	methyl glyoxal
	MACR	methacrolein
Acids	FACD	formic acid
	CCOOH	acetic acid
	RCOOH	higher organic acids and, in Carter, peroxy acids (mechanism based on propionic acid).
Other	ACYE	acetylene
	ACETONE	acetone
	MEK	ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 < 10^{-13}$ but slower than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}. (Based on mechanism for methyl ethyl ketone).
	PRD2	ketones and other non-aldehyde oxygenated products which react with OH radicals faster than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}.
	BACL	Biacetyl
	MVK	Methyl Vinyl Ketone
	MEOH	Methanol
	IPRD	Lumped isoprene product species

Table S7 The anthropogenic VOC emission species input into the RACM2 mechanism in the CMAQ model.

Mechanism	Category	Model Species	Definition
RACM2	Alkanes	ETH	ethane
		HC3	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12}
		HC3	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12}
		HC5	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) between 3.4×10^{-13} and 6.8×10^{-12}
		HC8	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) greater than 6.8×10^{-12}
	Alkenes	ETE	ethene
		API	alpha-pinenes and other cyclic terpenes with one double bond
		ISO	isoprene
		OLI	internal alkenes
		OLT	terminal alkenes

Aromatics	BEN	benzene
	CSL	cresol and other hydroxy substituted aromatics
	PHEN	phenol
	TOL	toluene and less reactive aromatics
	XYM	m-xylene
	XYP	p-xylene
	XYO	o-xylene
Aldehydes	ACD	acetaldehyde
	ALD	C3 and higher aldehydes
	BALD	benzaldehyde and other aromatic aldehydes
	GLY	glyoxal
	HCHO	formaldehyde
	MACR	methacrolein
	MGLY	methylglyoxal and other alpha-carbonyl aldehydes
	UALD	unsaturated aldehydes
Acids	ORA1	formic acid
	ORA2	acetic acid and higher acids
Other	ACE	acetylene
	ACT	Acetone
	EOH	ethanol
	KET	ketones
	MEK	methyl ethyl ketone
	MVK	methyl vinyl ketone
	MOH	methanol

(2) We argue that Fig. 9 should not be interpreted as a complete representation of the VOC distribution, for the reaction rate of OH radical with VOC is determined jointly by the OH concentration, VOC concentration, and the corresponding reaction rate constants.

(3) We placed Fig. 9 in Section 3.3 for a specific reason. After discussing the differences in O_3 formation among the three mechanisms driven by the RO_x-NO_x cycle, we aimed to further clarify whether the key emitted species affecting O_3 production under different NO_x regimes in Chengdu differ among the three chemical mechanisms. This issue is relevant to the formulation of control strategies for key VOC species. Therefore, in this section, we evaluated the differences in the reaction rates between OH and different categories of primary emitted VOC, for these reactions represent an important initiation pathway of the ROx cycle. However, we also recognize that the magnitude of the reaction rates of OH with VOC alone cannot fully quantify the contribution of primary emission of each VOC category to O_3 formation. For this, we further conducted CMAQ-DDM sensitivity simulations in Section 3.4 to identify the key primary VOC emissions influencing O_3 production under different NOx regimes in Chengdu for three chemical mechanisms. Therefore, we consider that Fig. 9 is more appropriately placed in Section 3.3, where it supports the discussion of the radical chain propagation of RO_x-NO_x cycle and further identify the key primary VOC emissions for different mechanisms.

4. **Comments:** *For the reader, it is challenging to connect all the results in the different subsections. In Section 3.2 it would help to interpret the results also based on the results presented in Section 3.2. Another example is Section 3.1.2 in which the impact of the strong overestimation of the measured OH radical concentration by the models is unclear. A too high simulated OH radical concentration leads to a faster VOC oxidation rate which may be the reason for or at least partly contributes to the underestimation of measured isoprene by the model.*

Reply: Thank you for your suggestion. We agree that the original manuscript did not sufficiently

explain the connections among the subsections. Regarding the connection between the two sections, our original intention was that Sections 3.1.2 and 3.1.3 were designed to evaluate the performance of different photochemical mechanisms from two distinct perspectives: key ozone precursors and atmospheric oxidation capacity, respectively. As for the connection of the results in the different subsections, the performance in simulated atmospheric radical concentrations among the chemical mechanisms cannot fully explain the biases in simulated precursor concentrations. Nevertheless, in order to better strengthen the connections between the subsections, we have tried our best to discuss and interpret the simulated precursor concentrations in light of the simulated atmospheric radical concentrations, such as the description of connection of the simulated reaction rates between OH and key primary VOC emissions and OH radical concentration:

"The lower OH-initiated oxidation rates simulated by CB06 for several major VOC classes are qualitatively consistent with its lower RO_2 concentrations (Fig. 5g-i, l)." Line 640-642

5. **Comments:** *Even though RO2 radical concentrations were not measured at the suburban site, the diurnal RO2 radical concentrations simulated by the different chemical mechanisms should be shown in Fig. 5 to get a full picture of the radical chemistry. It is unclear to the reader why measured and modelled HO2 radical concentrations agree very well but the OH radical concentration is so different. This hints towards different simulated HO2/RO2 ratios. What is the main difference in the RO2 chemistry of the three chemical mechanisms? Why does the SAPRC07 mechanism simulate a comparably high loss of ROx through HO2+RO2 (Fig. 8), even though RACM2 predicts similar HO2 and RO2 radical concentrations?*

Reply: Thank you for your suggestion.

(1) To provide a full picture of radical chemistry, we have added the diurnal variation in RO_2 radical concentrations at the XJ site (Fig. 5l), together with the corresponding description. In addition, to better illustrate the spatial distributions of the simulated radical concentrations during the peak period, we changed the time displayed for the simulated distribution of OH, HO_2, and RO_2 radical in Fig. 5 from 12:00 to 14:00 local time and updated the corresponding text accordingly. This change in plotting time does not affect the main conclusions of the study.

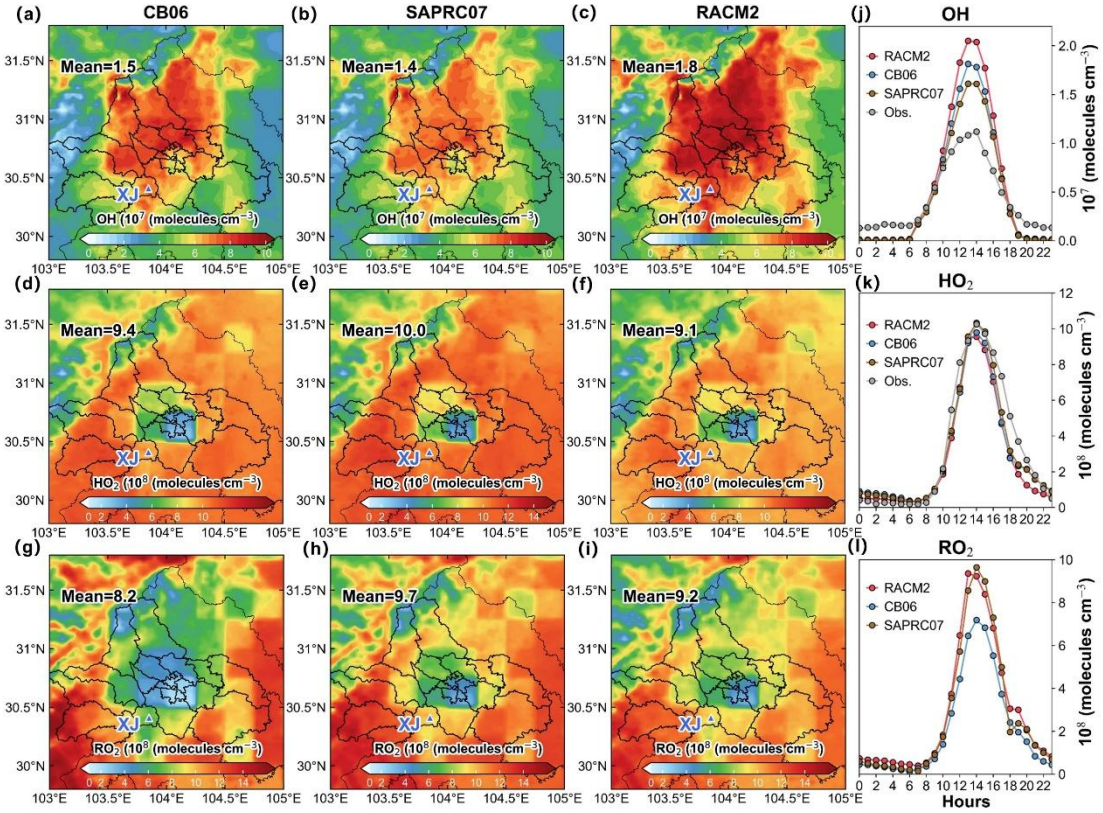


Figure 5 Regional distributions of OH, HO_2 and RO_2 radical concentration at 14:00 local time and diurnal variation at XJ site of OH, HO_2 and RO_2 concentration simulated by three photochemical mechanisms during August 9-August 18, 2019. The location of XJ site is marked with a dark blue triangle.

(2) Good agreement between simulated and observed HO_2 radical does not necessarily imply good agreement for OH radical, for that they are governed by different chemical production and loss pathways (Tan et al., 2019; Yang et al., 2021). Regarding the budget for OH radical budget, its production rate is quantified from the photolysis of HONO, photolysis of O_3, ozonolysis of alkenes and secondary production rates (dominated by HO_2 + NO and HO_2 + O_3). The destruction rate of OH radical is primarily calculated from the reaction rates of OH radical with NO_2, CO, O_3, SO_2 and VOC. Regarding the budget for the HO_2 radical, its production rate is quantified from the photolysis of HCHO, photolysis of other OVOC, ozonolysis of alkenes and secondary production rates (the conversion of OH with and RO_2).

(3) The main differences in RO_2 chemistry among the three chemical mechanisms can largely be attributed to differences in the lumping approaches for VOC precursors and RO_2 species, as well as in the relevant reaction rate constants and the calculation method of RO_2. First, the CBM was classified by carbon-bond structures (Luecken et al., 2019). SAPRC and RACM2 mechanism classifies organic species according to their OH reactivity and features the detailed description of reactions involving specific VOCs and they have different criteria for classification by OH reactivity (Carter, 2010b; Goliff et al., 2013). Moreover, the three mechanisms differ in the categories of RO_2 species lumping. RACM2 preserves the carbon structure of emitted species, explicitly individual RO_2 species, and minimizes

reliance on lumped species. CBM and SAPRC lump RO_2 species and referred to as operators for radical cycles.

(4) The loss rate of ROx through HO_2 +RO_2 depends on the reaction rate constant of the chemical reaction HO_2 with RO_2 ($k_{RO_2+HO_2}$), the concentrations of HO_2 and RO_2 radical, as shown below. Therefore, although the RACM2 and SAPRC07 chemical mechanisms yield similar simulated concentrations of HO_2 and RO_2, the termination rates of RO_x radicals via the HO_2 + RO_2 reaction differ between the two mechanisms, owing to differences in $k_{RO_2+HO_2}$, RO_2 lumping schemes and so on.

6. **Comments:** *Details about meteorological parameters (temperature, relative humidity, jNO2) and instruments measuring the trace gases are missing in the site description (Section 2.1).*

Reply: Thank you for your suggestion.

(1) We have added the details of instruments measuring trace gases in this revised manuscript.

"The trace gases include O3, NOx, isoprene (ISOP), nitric acid (HNO_3) and nitrous acid (HONO) at the urban site (SAES), and O3, NOx, HONO, ISOP, and formaldehyde (HCHO) at the suburban site (XJ). The details of instruments for measuring trace gases are summarized in Table S2." Line 169-172

Table S2 The details of instruments for measuring trace gases in this study.

Parameters	Method	Time resolution	Accuracy (%)	Limit of detection
O_3	UV absorption	1 min	± 5	0.5 ppbv
NO, NO_2	Chemiluminescence	1 min	± 20	0.5 ppbv 300 ppbv
VOC	GC–MS/FID[1]	1 h	± (Burling et al., 2010)	20–300 pptv
Formaldehyde	Hantzsch fluorimetry	1 min	±5	25 pptv
HNO_3	GAC-IC[2]	1 h	±5	0.13 μg/m³
HONO	Long-path absorption photometry	300 s	300 s ±20	10 pptv 10 pptv ±20%

Note. [1] GC–MS/FID is Gas Chromatography with Mass Spectrometry/with Flame Ionization Detection. [2] Gas and Aerosol Collector coupled with Ion Chromatography.

(2) In addition, we also have supplemented the observed meteorological parameters (temperature, relative humidity and wind speed) and evaluated of the performances of WRF in simulating these parameters, including error statistics (Table S9) and time-series plots comparing simulated and observation (Figure S3-5). The relevant analysis and discussion of performances of simulated meteorological parameters have also been incorporated into the revised manuscript. Given that direct observations of j(NO_2) were not available and the values of j(NO_2) were calculated by the module of in-line calculation of photolysis rates in the CMAQ, there is no evaluation for j(NO_2).

"Hourly meteorological parameters and trace gases were obtained. The meteorological parameters

included wind speed at 10 m (WS10M), temperature at 2 m (T2M) and relative humidity (RH).” Line 168-169

“The WRF simulation was evaluated against meteorological observations of T2M, RH and WS10M at the SAES and XJ sites. The corresponding time series was shown in Figure S3-S5 and model performance was further quantified using correlation coefficient (R), mean bias (MB), root-mean-square error (RMSE), and gross error (GE). The definitions and calculation formulas for these metrics are provided in Table S8, and the corresponding evaluation results are summarized in Table S9. The WRF simulation generally captured the observed variations in T2M and RH, with correlation coefficients ranging from 0.81 to 0.93. The RMSEs for WS10M (1.4–1.6 m s^{-1}) were below the commonly benchmark of 2.0 m s^{-1} suggested by (Emery and Tai, 2001). Moreover, compared to previous studies (T2M: 2.8 ≤ RMSE ≤ 3.3 K, RH: 14.3% ≤ RMSE ≤ 16.2% and 11.0% ≤ GE ≤ 12.6%, WS10M: 0.5 m s^{-1} ≤ MB ≤ 1.1 m s^{-1} and 1.8 m s^{-1} ≤ RMSE ≤ 2.3 m s^{-1}) over SCB in summer (Qiao et al., 2019), the statistical indices of T2M (2.2 K ≤ GE ≤ 3.1 K), RH (10.6% ≤ RMSE ≤ 12.6% and 8.1% ≤ GE ≤10.3%) and WS10M (-0.3 m s^{-1} ≤ MB ≤ 0.9 m s^{-1} and 1.4 m s^{-1} ≤ RMSE ≤1.6 m s^{-1}) in this study was closer to observation. Overall, the simulated meteorological fields provided a reasonable basis for the subsequent CMAQ simulations.” Line 207-220

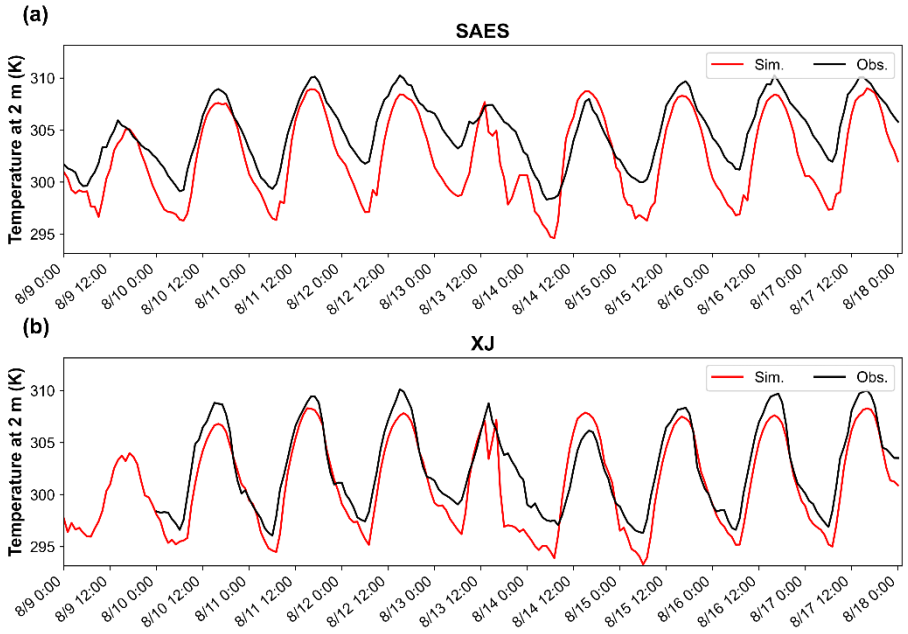


Figure S3 Time series of temperature (K) at 2 m simulation (red lines) and observation (black lines) at SEAS (a) and XJ (b) sites.

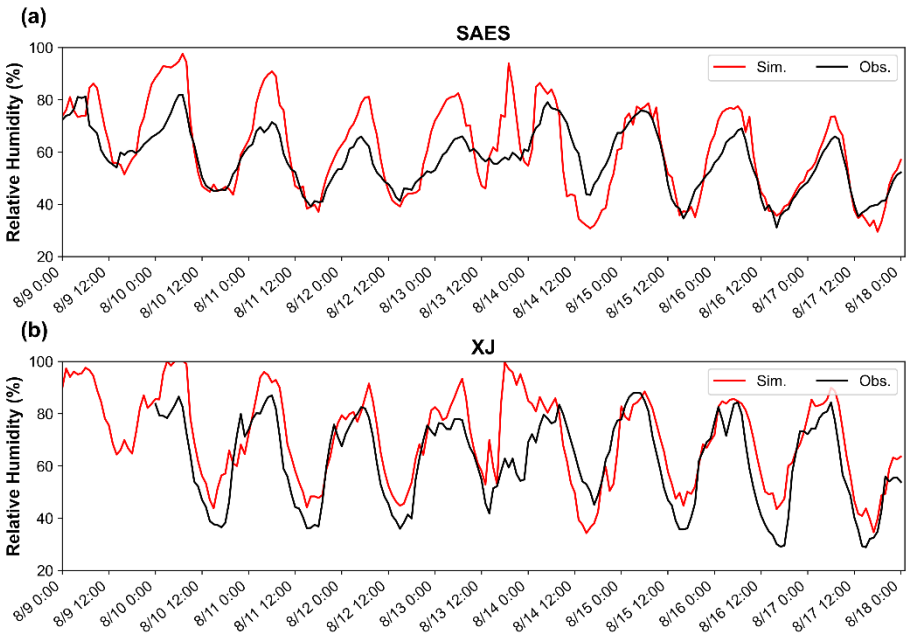


Figure S4 Time series of relative humidity (%) simulation (red lines) and observation (black lines) at SEAS (a) and XJ (b) sites.

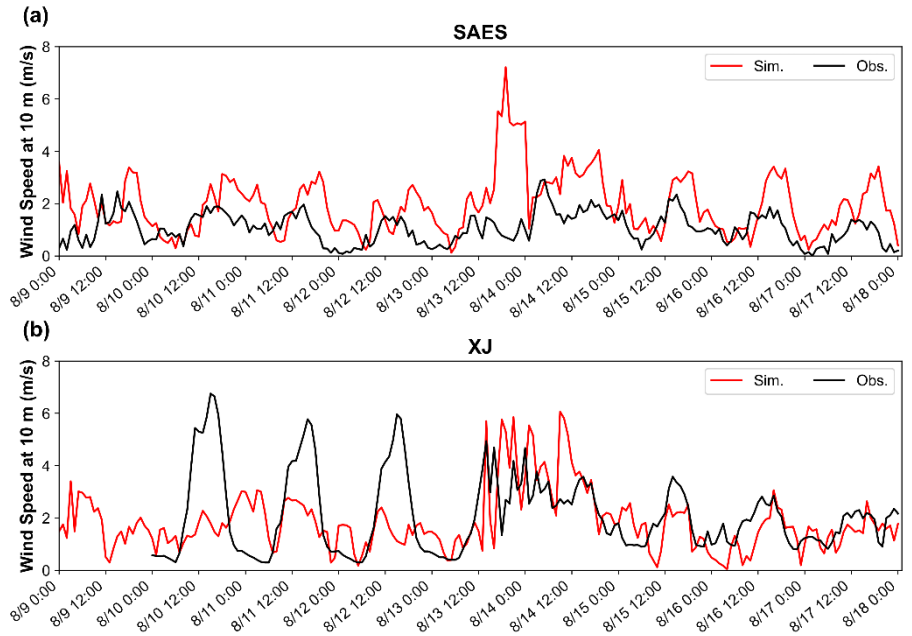


Figure S5 Time series of wind speed (m/s) at 10 m simulation (red lines) and observation (black lines) at SEAS (a) and XJ (b) sites.

Table S8 Statistical metrics for photochemical mechanisms performance evaluation discussed in this study.

Statistic/abbreviation	Definition	Notes

Correlation coefficient (R)	$\frac{\sum[(S_i-\bar{S})\times(O_i-\bar{O})]}{\sqrt{\sum(S_i-\bar{S})^2\times\sum(O_i-\bar{O})^2}}$	-1≤R≤1
Index of Agreement (IOA)	$1-\frac{\sum(S_i-O_i)^2}{\sum(\lvert S_i-\bar{O}\rvert+\lvert O_i-\bar{O}\rvert)^2}$	0≤IOA≤1
Mean Fractional Bias (MFB)	$\frac{2}{N}\sum\frac{(S_i-O_i)}{(S_i+O_i)}\times 100$	-200%≤MFB≤+200%
Mean Fractional Error (MFE)	$\frac{2}{N}\sum\frac{\lvert S_i-O_i\rvert}{(S_i+O_i)}\times 100$	0≤MFE≤+200%
Root Mean Square Error (RMSE)	$\frac{\sqrt{\frac{1}{N}\sum(S_i-O_{i)}{}^2}}{\sqrt{\frac{1}{N}\sum[(S_i-\bar{S})-(O_i-\bar{O})]^2}}$	/
Gross Error (GE)	$\frac{2}{N}\sum\lvert S_i-O_i\rvert$	/

Note. Subscript i represents the pairing of N observations O and simulations S by site and time. Overbars signify means over site and/or time.

Table S9 The WRF model performance for temperature (°C) at 2 m, relative humidity (%) at 2 m, wind speed (m/s) at SAES and XJ site.

	Obs.	**Sim.**	**R**	**MB**	**RMSE**	**GE**
2-m Temperature (K)						
SAES	302.4	304.8	0.9	-2.4	3.1	2.7
XJ	301.0	302.7	0.93	-1.5	2.2	1.8
2-m Relative Humidity (%)						
SAES	60.7	57.0	0.84	3.7	10.6	8.1
XJ	70.5	61.7	0.81	7.2	12.6	10.3
10-m Wind Speed (m/s)						
SAES	2.0	1.1	0.32	0.9	1.4	1.0
XJ	1.9	2.1	0.32	-0.3	1.6	1.2

Note. R is correlation coefficient; MB is mean bias; RMSE is root mean square error; GE is gross error. The equations of R, MB, RMSE and GE can be found in Table S8.

Technical corrections

Overall, the language should be improved. Prepositions and articles are often missing.

1. **Comments:** *Line 13: It should be emphasized that surface/tropospheric ozone is simulated.*

Reply: Thank you for your suggestion. *We have revised the point.*

"Photochemical mechanisms are core components of air quality models, yet differences among them can introduce substantial uncertainty in tropospheric ozone (O_3) simulations." Line 12-13

2. **Comments:** *Line 17: The NOx conditions should be specified.*

Reply: Thank you for your suggestion. we have added a clear definition of NO_x, namely nitrogen oxides, at its first occurrence in the text.

"This contrasting response of O_3 concentrations to emission reductions is closely related to the highly nonlinear photochemical dependence of O_3 formation on its major precursors, nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs)." Line 47-48

3. **Comments:** *Lines 34-35: Ozone is typically not the main oxidant regulating atmospheric lifetimes. This of course depends on the boundary conditions. A large part of this paper focuses on the photochemical radical chemistry forming ozone, when the OH radical usually determines the removal of pollutants. The hydroxyl radical should be introduced as the main daytime oxidant in the troposphere driving the ozone formation during the day.*

Reply: Thank you for your suggestion. The oxidation capacity that determines atmospheric lifetimes is indeed predominantly governed by OH radicals, rather than by ozone. We realized that the description of ozone in the manuscript was inaccurate, and we have revised it accordingly based on your suggestion.

"Ozone (O_3) is a potent oxidant in the atmosphere, playing a key role in the oxidation of trace gases in the troposphere" Line 37-38

4. **Comments:** *Line 41: NOx was not introduced yet.*

Reply: Thank you for your suggestion. The original sentence has already been slightly revised. We have added a clear definition of NO_x, namely NO + NO_2, at its first occurrence in the main text.

"This contrasting response is closely related to the highly nonlinear photochemical dependence of O_3 formation on its major precursors, nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs)." Line 46-48

5. **Comments:** *Lines 47, 51: A verb is missing here: "In theory, once O3 is formed, …"*

Reply: Thank you for your suggestion. In accordance with Major Comment #1, we have already removed this part, so no further changes will be made here.

6. **Comments:** *Line 48: It is misleading that R1 to R3 are mentioned as an example.*

Reply: Thank you for your suggestion. To better understand the O_3 formation process and in accordance with Major Comment #1, we have reordered reactions R1-R3 in the Table S1 in the revised manuscript.

Reactions	**No.**
$NO_2 + h\nu\ (< 424\ nm) \rightarrow O(^3P) + M$	(R1)
$O(^3P) + O_2 + M \rightarrow O_3 + M$	(R2)
$O_3 + NO \rightarrow NO_2 + O_2$	(R3)

7. **Comments:** *Line 91-92: The reactions are not complete or false.*

Reply: Thank you for your suggestion. We have revised the reaction*s* in the updated manuscript, shown

in the Table S1.

Termination reactions of the RO_x cycle	
$OH + NO_2 \rightarrow HNO_3$	(R14)
$OH + NO \rightarrow HONO$	(R15)
$RO_2 + NO \rightarrow RONO_2$	(R16)
$RO_2 + RO_2 \rightarrow products$	(R17)
$RO_2 + HO_2 \rightarrow ROOH + O_2$	(R18)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(R19)
$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2$	(R20)

8. **Comments:** *Line 135: A quantitative comparison would be beneficial here.*

Reply: Thank you for your suggestion. We have added the quantitative comparison in the manuscript. "Over Japan, mechanism-dependent O_3 differences reached 10 ppb, with CB05TUCL generally lower than SAPRC07TC and RACM2 close to SAPRC07TC (Kitayama et al., 2019). Similarly, SAPRC07 and RACM2 yielded higher summer O_3 than CB6R3 in Alberta, accompanied by OH increases of about 30% and 100%, respectively (Shareef et al., 2022)" Line 109-112

9. **Comments:** *Line 142: References are missing.*

Reply: Thank you for your suggestion. We further realized that our previous summarization was indeed incomplete and imprecise. To address this, we have thoroughly revised the text in the revised manuscript, rephrased the description, and incorporated several references.

"Despite these advances, the influence of different photochemical mechanisms on three-dimensional O_3 simulations over China remains poorly constrained, and systematic evaluations of the resulting uncertainty are still scarce (Huang et al., 2025; Liu et al., 2023)." Line 122-124

10. **Comments:** *1a: The position of the XJ site is not visible as it has the same color as the map. It would be consistent to plot the NOx values in b in the same colors as the locations in plot a.*

Reply: Thank you for your suggestion. We have made the following visual improvements in the revised manuscript: The XJ and SAES site markers in Figure 1a has been recolored to make it clearly distinguishable from the background and better match the site colors used in Figure 1b. This modification ensures that readers can easily cross-reference the spatial locations with their corresponding NO_x values.

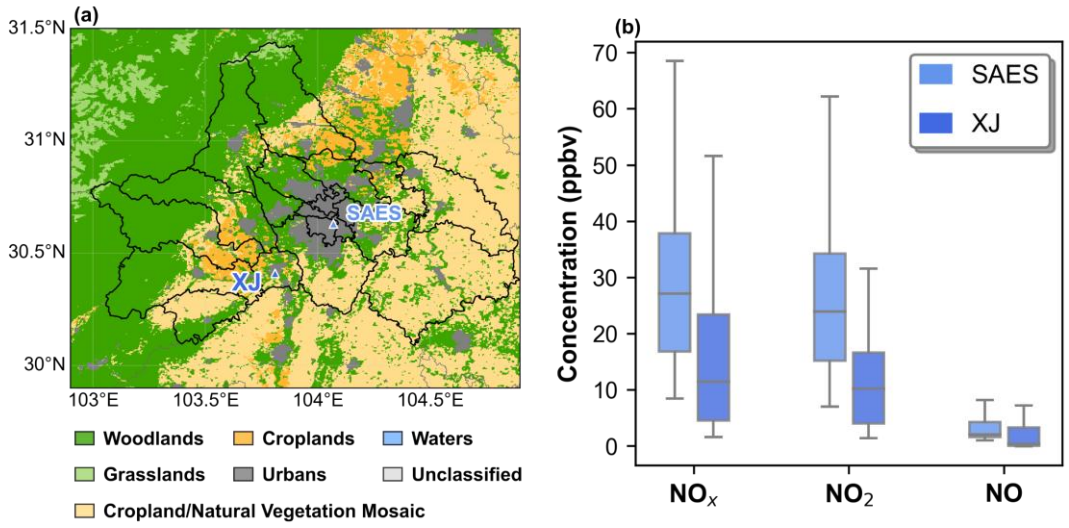


Figure 1 (a) Land use types in Chengdu and surrounding areas, along with the locations of the SAES site (light blue triangle) and XJ site (dark blue triangle). (b) Distribution of NO_x (NO_x = NO +NO_2), NO_2 and NO concentrations (ppbv) at the Sichuan Academy of Environmental Sciences (SAES) site and Xinjin (XJ) site during this pollution episode. The box plots present the 10th, 25th, 50th, 75th, and 90th percentiles of the statistical metrics individually.

11. **Comments:** *Line 192: Add Fuchs et al. (Rev. Sci. Instrum. 8, 084104 (2008))*

Reply: Thank you for your suggestion. The reference to Fuchs et al. (2008) for the LIF detection of tropospheric RO_2 and HO_2 radicals has been added in the revised manuscript.

"which utilizes the fluorescence assay by gas expansion (FAGE) technique (Fuchs et al., 2008)" Line 174-175

12. **Comments:** *Line 234: References to the reactions help here.*

Reply: Thank you for your suggestion. We have supplemented the manuscript with relevant reference.

"However, in the real atmosphere, other key oxidizing agents such as HO_2 and RO_2 radicals in the troposphere can also oxidize NO to NO_2 (Monks, 2005). The combination of these reactions (R1-2 and R11-12 in Table S1) lead to net O_3 production in the troposphere (Tan et al., 2018)." Line 237-239

13. **Comments:** *Line 242: The fraction of RO2+NO forming organic nitrate should be excluded here.*

Reply: Thank you for your suggestion. In the actual analysis of manuscript, we indeed considered only the fraction of RO_2 + NO forming NO_2 (which produces NO_2 and thus contributes to ozone formation), while the channel leading to organic nitrates was explicitly omitted. However, we also recognize that the original description in the manuscript was not sufficiently clear on this matter. To address this, we have revised the manuscript to state this explicitly. The amended sentence now reads:

"Following this mechanism, the gross O_3 formation rate ($F(O_3)$) given approximately by the rate at which the HO_2 and each RO_2 radicals species i oxidize NO to NO_2 is calculated using Equation (1), where k represents the bimolecular reaction rate constant." Line 239-243

14. **Comments:** *Line 243: Only O1D+H2O forming 2OH should be considered in the first term.*

Reply: Thank you for your suggestion. We agree that only $O(^1D) + H_2O \rightarrow 2OH$ should be included in the first term of the ozone budget. In our actual analysis, we indeed included only this reaction in the first term. However, we recognize that our original description in the manuscript was not explicit. To clarify, we have made supplementary descriptions in the revised manuscript.

"Conversely, O_3 loss pathways include O_3 photolysis to $O(^1D)$ (followed by the reaction of $O(^1D)$ with water vapor) and ozonolysis of alkenes, and reactions with OH and HO_2. Additionally, the reaction of NO_2 with OH, which effectively removes NO_x from the cycle by forming HNO_3, is also accounted for one of the O_3 loss pathways. The total O_3 destruction rate ($D(O_3)$) is determined by Equation (2).

$$D(O_3) = j_{O^1D}[O_3] \times fac + k_{[O_3,Alkenes]}[Alkenes][O_3] + k_{[O_3,OH]}[O_3][OH] + k_{[O_3,HO_2]}[O_3][HO_2] + k_{[NO_2,OH]}[NO_2][OH] \quad (2)$$

$$fac = \frac{k_{[O(^1D),H_2O]}[H_2O]}{\left(k_{[O(^1D),O_2]}[O_2] + k_{[O(^1D),N_2]}[N_2] + k_{[O(^1D),H_2O]}[H_2O]\right)}$$

It noted that the first term for O_3 photolysis in Equation (2) is only including the reaction of $O(^1D)$ with H_2O to generate OH, which leads to net O_3 loss. Other $O(^1D)$ loss channels (e.g., quenching by N_2 or O_2) regenerate O_3 through $O(^3P) + O_2$ and thus have no net effect on O_3 destruction, resulting in that they are excluded from this term accordingly." Line 244-251

15. **Comments:** *Figure 3: The abbreviations should be introduced.*

Reply: Thank you for your suggestion. All abbreviations in the Figure 3 are now defined at their first appearance in the text and figure caption.

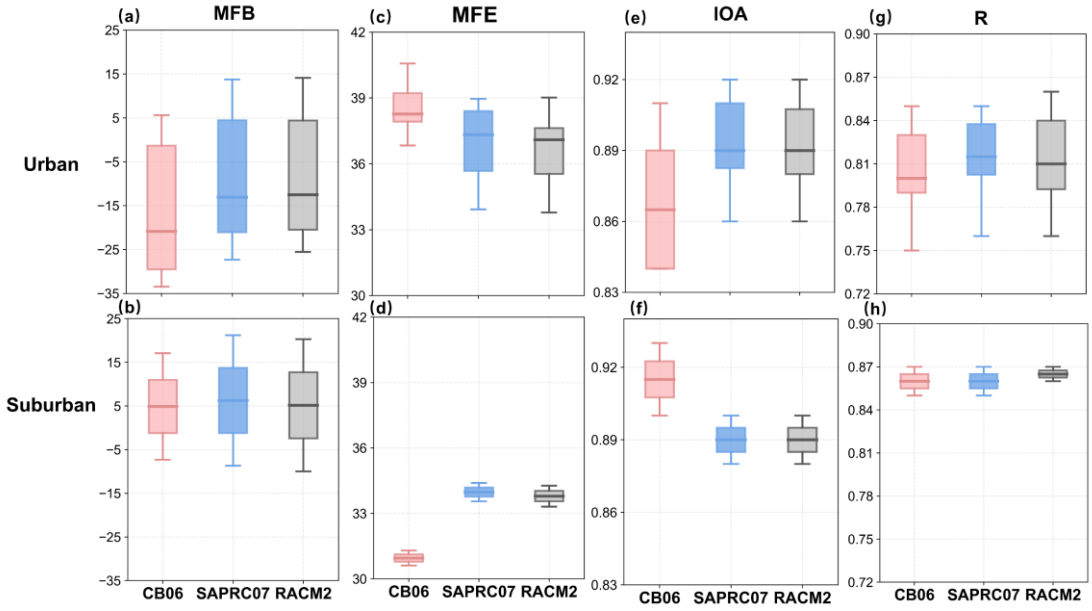


Figure 2 Statistical analysis of hourly O_3 simulated by three photochemical mechanisms (CB06, SAPRC07 and RACM2) s at urban sites and suburban sites across Chengdu region during August 9-August 18, 2019. The box plots present the 10th, 25th, 50th, 75th, and 90th percentiles of the statistical metrics individually. The statistical metrics, including mean fractional bias (MFB), mean fractional error (MFE), index of agreement (IOA)

and correlation coefficient (R), are presented. MFB and MFE are given as percentages. The unit of MFB and MFE is percent (%).

"The performance of the three photochemical mechanisms in simulating O_3 pollution was further evaluated using the mean fractional bias (MFB), mean fractional error (MFE), index of agreement (IOA), and R, to evaluate the discrepancies between simulated results and observed values (Fig. 3)." Line 305-307

16. **Comments:** *Figure 4: Is there a reason why the model-measurement comparison of NO is missing?*

Reply: Thank you for your suggestion. We have supplemented the model-measurement comparison of NO into the Figure 4 in the revised manuscript.

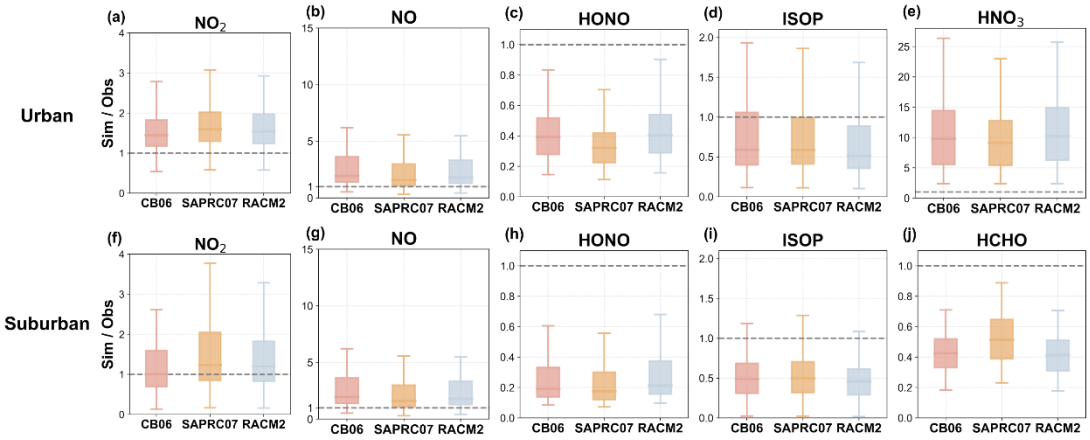


Figure 3 Comparison of three photochemical mechanisms on key photochemical species at urban site and suburban site. The box plots present the 10th, 25th, 50th, 75th, and 90th percentiles of the ratio of simulation value vs observation value (08:00-18:00 local time) individually.

"The simulated NO exhibited a more pronounced site-dependent simulation bias than NO_2 (Fig. 4b, g). At the urban site, the median simulated-to-observed NO ratios for CB06, RACM2, and SAPRC07 were 2.0, 1.8, and 1.6, respectively. These values indicated that all three mechanisms overestimated NO, with SAPRC07 showing the lowest median bias. At the suburban site, the corresponding median ratios were 2.1, 2.2, and 1.9, respectively. The ratio distributions at the suburban site were also substantially broader and exhibited pronounced upper tails, reflecting greater variability and severe overestimation. Overall, SAPRC07 yielded the lowest median bias at both sites, although none of the three mechanisms eliminated the positive bias in NO simulations, particularly at the suburban site. Consistent with previous studies, the overall performance of current air quality models in simulating NO remains limited (Kaynak et al., 2013). The bias may be associated with the uncertainties of emission inventories (Pennington et al., 2024) and the effects of numerical diffusion on simulated chemical processes (Zhu et al., 2024)." Line 358-368

17. **Comments:** *Line 337-338: It sounds like the HCHO photolysis is the main radical source which is not true. Naming the relative contribution to P(ROx) will clarify its role.*

Reply: Thank you for your suggestion.

1） The original description at Lines 337-338 was indeed imprecise and may have inadvertently overstated the role of HCHO photolysis as a primary radical source. To address this, we have revised the relevant text accordingly. In the revised manuscript, we have not only clarified the description but also supplemented the references to the relative contribution of HCHO photolysis to the primary RO_x production rate reported in previous studies.

"Previous studies have shown that HCHO photolysis can contribute approximately 10%–34% of primary RO_x production in China (Lu et al., 2013; Tan et al., 2017; Tan et al., 2019; Xue et al., 2016)," Line 400-402

2） As this section focuses on the simulation performance of different chemical mechanisms for HCHO, we do not elaborate on the contributions of HCHO photolysis to $P(RO_x)$ here; instead, these results are described in detail in the Section 3.3.1. Based on simulations using the three chemical mechanisms, HCHO photolysis contributed 11.2–16.3% of primary RO_x production at urban site (Lines 537) and 13.6–18.9% at suburban site (Line 547) in Chengdu.

18. **Comments:** *Figure 5: The columns are not labelled with the corresponding mechanism shown. Furthermore, it should be reminded that XJ is the suburban site. In the colour maps, it would be helpful to add the measurement point, similar to Fig. 2.*

Reply: Thank you for your suggestion. We have added mechanism labels at the top of each column in Figure 5. Moreover, we have added a triangle to the color maps in Figure 5, using the same style as in Figure 2, to pinpoint the location of XJ site. The revised Figure 5 has been redrawn and the caption has been updated accordingly.

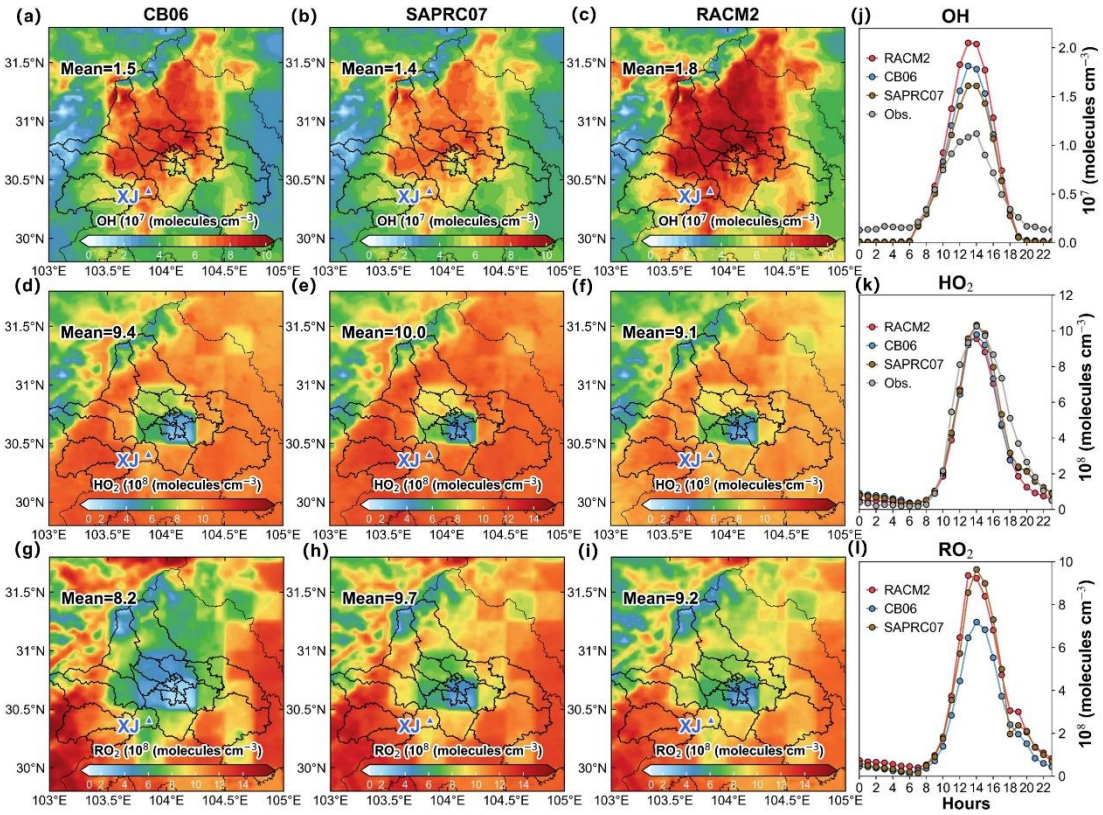


Figure 5 Regional distributions of OH, HO_2 and RO_2 radical concentration at 14:00 local time and diurnal variation at XJ site of OH, HO_2 and RO_2 concentration simulated by three photochemical mechanisms during August 9-August 18, 2019. The location of XJ site is marked with a dark blue triangle.

Reviewer: 2

General comments: *This manuscript evaluates the dependence of simulated ozone formation and precursor sensitivity on three gas-phase chemical mechanisms (CB06, SAPRC07, and RACM2) using CMAQ during an ozone pollution episode in Chengdu. The topic is relevant to atmospheric chemistry and air-quality modeling and falls within the scope of ACP. A systematic comparison of mechanism-dependent ozone formation, radical chemistry, and precursor sensitivity under contrasting urban and suburban NOx conditions could potentially provide useful insight into chemical-mechanism uncertainty in regional air-quality simulations.*

However, in its current form, the manuscript does not provide the scientific depth, methodological rigor, or level of mechanistic interpretation needed to realize this potential. Much of the Results and Discussion consists of restating values, rankings, and fractional contributions already shown in the figures, with limited analysis of why CB06, SAPRC07, and RACM2 produce different results. Conversely, several chemical explanations are speculative and are not supported by direct model diagnostics or quantitative evidence. Important methodological issues - including differences in the accompanying model configurations, evaluation of the customized RACM2 emission mapping, limited description of mechanism-specific chemical differences, incomplete measurement documentation, and the lack of meteorological model evaluation - further prevent a robust interpretation of the inter-mechanism comparison.

The manuscript also requires substantial reorganization and comprehensive English-language editing. Frequent grammatical errors, awkward or unclear expressions, repeated textbook-level explanations, and poorly structured paragraphs substantially impede readability and, in several places, obscure the intended scientific meaning. These concerns are not limited to isolated sections that could be addressed through routine revision; rather, they affect the analysis, interpretation, scientific contribution, and presentation of the manuscript as a whole. Although the subject is within the scope of ACP, I do not consider the manuscript suitable for publication in its present form. I therefore recommend rejection, while leaving open the possibility of a substantially redeveloped manuscript being considered as a new submission.

Reply: Thank you very much for your careful review and valuable comments. We have tried our best to revise the manuscript according to your comments. The corrections in the manuscript are marked in blue.

The detailed comments supporting this assessment are provided below.

General comments:

1. **Comments:** *A major limitation of the manuscript is that much of the Results and Discussion remains*

descriptive rather than mechanistic. Many sections primarily restate values, rankings, or relative contributions shown in the figures, while the chemical reasons for the differences among CB06, SAPRC07, and RACM2 are not sufficiently investigated. Conversely, several mechanistic explanations are proposed speculatively without direct evidence from the simulations. The authors should provide quantitative support for their interpretations and more explicitly connect the observed differences to mechanism-specific features, including VOC lumping/speciation, reaction pathways and rate parameters, radical production and propagation, and RO2 composition and fate. Without such analysis, it is difficult to determine why the mechanisms behave differently or to assess the broader scientific significance of the inter-comparison.

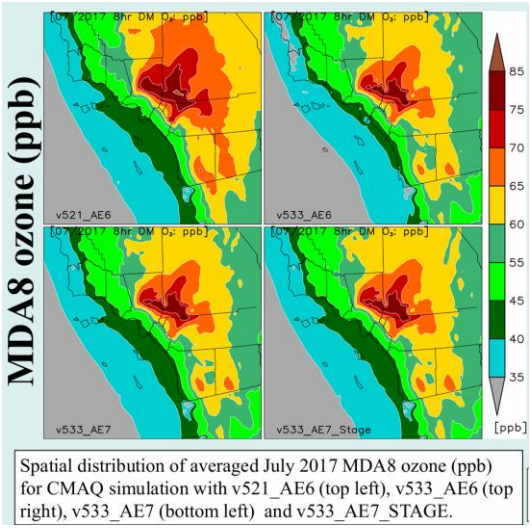
Reply: Thank you for your suggestion. In the revised manuscript, we have substantially strengthened the mechanistic interpretation of the inter-mechanistic differences among CB06, SAPRC07, and RACM2, rather than relying primarily on descriptive comparisons of simulated concentrations and reaction contributions. Specifically, we have added quantitative analyses linking differences in O_3 and RO_x cycle to major formation and loss pathways. We further connected these differences to mechanism-specific features such as reaction rate parameters, radical concentrations, and RO_2-related chemistry. Statements that were previously speculative have also been revised or qualified according to the available evidence. Detailed quantitative analyses and corresponding revisions are provided in the revised manuscript.

2. **Comments:** *The manuscript does not yet demonstrate that the reported differences arise specifically from the gas-phase mechanisms. The three simulations use different accompanying CMAQ configurations, including different aerosol modules, and RACM2 relies on a customized VOC emission mapping. The authors should quantitatively evaluate conservation of total VOC emissions, carbon mass, and VOC reactivity in the mapping, clarify the influence of the accompanying configurations, and provide a systematic comparison of relevant mechanism-specific chemistry. These details are necessary for interpreting differences in simulated radicals and ozone.*

Reply: Thank you for your suggestion. We examined the impacts of several factors on the simulation results.

1) the impact of aerosol modules

Kulkarni et al. (2021) previously reported that different aerosol module versions (AERO6 and AERO7) in the CMAQ model have little impact on ozone simulations over the United States, with the results showing that the two versions have a negligible effect on MDA8 O_3 over inland areas, while only slight differences were observed along the coastal regions (shown as Response Figure 1). Since the Sichuan Basin targeted in our study is an inland region, it can be inferred that the influence of AERO6 and AERO7 on ozone simulations over this basin is likewise negligible. Furthermore, compared to AERO7, AERO7i only provides more the diagnostic information in terms of IEPOX SOA identity, as well as some minor additional high-NOx pathways to SOA (a particle-phase isoprene dinitrate and does not materially affect the simulation results (Appel et al., 2021). Therefore, the effects of different aerosol module versions (AERO6, AERO7, and AERO7i) on ozone simulations in this study can be negligible.



Response Figure 1. Spatials distribution of averaged July 2017 MDA8 ozone (ppb) for CMAQ with different aerosol module versions. Adapted from Kulkarni, S. (2021).

Kulkarni, Sarika. “California Air Resources Board Testing Internally Compressed NetCDF-4 File Format within SMOKE-IOAPI Framework.” Presentation slides presented at the CMAS Conference 2021, 2021.https://www.cmascenter.org/conference/2021/slides/kulkarni-cmaq5-3-2-california-2021.pdf

2) the impact of emission mapping

we carefully considered this issue in the simulation design. First, all emissions were based on the same version of the MEIC inventory and MEGAN, ensuring consistency in the emission source strengths. Second, for explicit VOC species shared by different chemical mechanisms, such as benzene, ethene, isoprene, and glyoxal, we checked the emission totals in the inventory item by item and ensured that they were identical across mechanism simulations. This eliminates emission-related uncertainty for these explicit species. Third, for lumped VOC species, we applied consistent mapping principles as far as possible, based on criteria such as carbon-bond structure, reactivity, and functional groups, so that the mapping rules remained comparable among mechanisms. Nevertheless, since the methods of different chemical mechanisms lumping VOC species is inconsistent, some differences in the mapping VOC speciates are unavoidable. This uncertainty originates from the theoretical species-definition framework of each mechanism and cannot be completely removed during emission preprocessing. However, by applying the unified mapping principles described above, we minimized its influence on the comparability of the results.

In addition, Fig. 9 also indirectly supports the reasonableness of the emission-mapping strategies used in this study, for that the reaction rates of OH with the major primary-emission VOC categories are generally similar among the three mechanisms. Although the OH reaction rate with alkanes is slightly higher in the CB06 mechanism than in the other two mechanisms, this mainly results from the mapping of more species into the PAR category, which represents carbon-carbon single bonds in CB06. Since alkanes are relatively less reactive, a higher OH reaction rate with alkanes does not necessarily imply a

substantial effect on O_3 simulation. Therefore, we consider that the mapping strategies do not materially affect the key conclusions of this study. In addition, to provide a clearer description of the emission mapping process for different photochemical mechanisms, we have split the original Table S5 into Tables S5-S7, which present the categories of emission species for each photochemical mechanism in the CMAQ.

Table S5 The anthropogenic VOC emission species input into the CB06 mechanism in the CMAQ model.

Mechanism	Category	Model Species	Definition
CB06	Alkanes	ETHA	ethane
		PRPA	propane
		PAR	carbon-carbon single bond
	Alkenes	ETH	ethene (ethylene)
		OLE	terminal alkene bond
		IOLE	internal alkene bond
		ISOP	isoprene
		TERP	monoterpenes
	Aromatics	BENZENE	benzene
		TOL	toluene and other monoalkyl aromatics
		XYLMN	xylene and other polyalkyl aromatics except naphthalene
		CRES	cresol and higher molecular weight phenols
	Aldehydes	FORM	formaldehyde
		ALD2	acetaldehyde
		ALDX	aldehydes with 3 or more carbons
		GLY	glyoxal
		MGLY	methyl glyoxal
	Acids	FACD	formic acid
		AACD	acetic acid
	Others	ETHY	ethyne (acetylene)
		ACET	acetone
		ISPD	isoprene reaction products (methacrolein, methylvinyl ketone, others)
		MEOH	methanol
		ETOH	ethanol
		KET	carbon-ketone bond

Table S6 The anthropogenic VOC emission species input into the SAPRC07 mechanism in the CMAQ model.

Mechanism	Category	Model Species	Definition
SAPRC07	Alkanes	ALK1	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 2 and 5 × 10^2 ppm^{-1} min^{-1}. (Primarily ethane)
		ALK2	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 5 × 10^2 and 2.5 × 10^3 ppm^{-1} min^{-1}. (Primarily propane and acetylene)
		ALK3	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 2.5 × 10^3 and 5 × 10^3 ppm^{-1} min^{-1}.

	ALK4	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} between 5×10^3 and 1×10^4 ppm^{-1} min^{-1}.
	ALK5	alkanes and other non-aromatic compounds that react only with OH, and have k_{OH} greater than 1×10^4 ppm^{-1} min^{-1}.
Alkenes	ETHE	Ethene
	OLE1	alkenes (other than ethene) with $k_{OH} < 7 \times 10^4$ ppm^{-1} min^{-1}.
	OLE2	Alkenes with $k_{OH} > 7 \times 10^4$ ppm^{-1} min^{-1}.
	ISOP	isoprene
	TERP	terpenes
Aromatics	ARO1	aromatics with $k_{OH} < 2 \times 10^4$ ppm^{-1} min^{-1}.
	ARO2MN	ARO2 minus naphthalene
	BENZENE	benzene
	CRES	phenols and cresols
Aldehydes	HCHO	formaldehyde
	CCHO	acetaldehyde
	RCHO	lumped C3+ aldehydes (mechanism based on propionaldehyde)
	BALD	aromatic aldehydes (e.g., benzaldehyde)
	GLY	glyoxal
	MGLY	methyl glyoxal
	MACR	methacrolein
Acids	FACD	formic acid
	CCOOH	acetic acid
	RCOOH	higher organic acids and, in Carter, peroxy acids (mechanism based on propionic acid).
Other	ACYE	acetylene
	ACETONE	acetone
	MEK	ketones and other non-aldehyde oxygenated products which react with OH radicals faster than $5 < 10^{-13}$ but slower than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}. (Based on mechanism for methyl ethyl ketone).
	PRD2	ketones and other non-aldehyde oxygenated products which react with OH radicals faster than 5×10^{-12} cm^3 $molec^{-2}$ sec^{-1}.
	BACL	Biacetyl
	MVK	Methyl Vinyl Ketone

	MEOH	Methanol
	IPRD	Lumped isoprene product species

Table S7 The anthropogenic VOC emission species input into the RACM2 mechanism in the CMAQ model.

Mechanism	Category	Model Species	Definition
RACM2	Alkanes	ETH	ethane
		HC3	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12}
		HC3	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12}
		HC5	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) between 3.4×10^{-13} and 6.8×10^{-12}
		HC8	alkanes, esters and alkynes with OH rate constant (298 K, 1 atm) greater than 6.8×10^{-12}
	Alkenes	ETE	ethene
		API	alpha-pinenes and other cyclic terpenes with one double bond
		ISO	isoprene
		OLI	internal alkenes
		OLT	terminal alkenes
	Aromatics	BEN	benzene
		CSL	cresol and other hydroxy substituted aromatics
		PHEN	phenol
		TOL	toluene and less reactive aromatics
		XYM	m-xylene
		XYP	p-xylene
		XYO	o-xylene
	Aldehydes	ACD	acetaldehyde
		ALD	C3 and higher aldehydes
		BALD	benzaldehyde and other aromatic aldehydes
		GLY	glyoxal
		HCHO	formaldehyde
		MACR	methacrolein
		MGLY	methylglyoxal and other alpha-carbonyl aldehydes
		UALD	unsaturated aldehydes
	Acids	ORA1	formic acid
		ORA2	acetic acid and higher acids
	Other	ACE	acetylene
		ACT	Acetone
		EOH	ethanol
		KET	ketones
		MEK	methyl ethyl ketone
		MVK	methyl vinyl ketone
		MOH	methanol

3. **Comments:** *The manuscript requires substantial English-language editing and reorganization. The Introduction contains frequent grammatical errors, awkward sentence structures, incorrect article and verb usage, and expressions that obscure the intended meaning. Similar issues occur elsewhere. Several Results subsections also combine general findings, numerical description, and interpretation without clear paragraph structure. The technical corrections below identify examples but are not exhaustive. All authors should carefully review the entire manuscript, simplify overly long or repetitive passages, and obtain editing by a fluent scientific English speaker.*

Reply: Thank you for your suggestion. The entire manuscript has been carefully revised for English

grammar, sentence structure, terminology, and overall readability.

Specific comments:

1. **Comments:** *Lines 45-93: The description of fundamental ozone and ROx-NOx chemistry is overly detailed for the Introduction, including numerous elementary reactions that constitute textbook knowledge. This section could be substantially condensed, allowing greater emphasis on how differences in VOC lumping, radical propagation, reaction rate coefficients, and termination pathways among CB06, SAPRC07, and RACM2 may influence modeled ozone formation and precursor sensitivity.*

Reply: Thank you for your suggestion. We have substantially condensed the fundamental O_3 and RO_x-NO_x chemistry in the Introduction. In addition, following the reviewer's advice, we further focus on the key differences among the three mechanisms—CB06, SAPRC07, and RACM2, with particular emphasis on how the representation of RO_2 radical chemistry influences modeled ozone formation and precursor sensitivity. Specifically, we have added the following discussion:

"However, the representation of RO_2 chemistry in CBM remains highly lumped, employing a single generic surrogate (e.g., XO_2) to approximate the collective reactivity of structurally diverse alkyl peroxy radicals, while a few key species (e.g., toluene peroxy radical, acetylperoxy radical) are treated explicitly (Zaveri and Peters, 1999)." Line 81-86

"And SAPRC mechanism achieves a deliberate balance between computational efficiency and chemical complexity through its chemical operator approach (Carter, 2010b; Carter, 2010a). However, although this chemical operator method offers advantages in computational efficiency, it sacrifices chemical specificity in distinguishing RO_2 radicals derived from specific VOC precursors and thereby impedes the accurate quantification of RO_2 production attributable to individual precursor VOCs." Line 89-95

2. **Comments:** *Reaction R2: NO is missing from the products of NO2 photolysis.*

Reply: Thank you for your suggestion. In the revised manuscript, following the reviewer's earlier suggestion, we have removed Reaction R2 from the main text. The correct reaction is described in Table S1 of the Supporting Information, as shown in R1.

$$NO_2 + h\nu\ (< 424\ nm) \rightarrow O(^3P) + NO \qquad \text{(R1)}$$

3. **Comments:** *Reaction R9: The reaction as written represents only H abstraction. OH addition to alkenes or aromatics does not produce H2O. Please revise the generalized VOC + OH reaction accordingly.*

Reply: Thank you for your suggestion. In the revised manuscript, following the reviewer's earlier suggestions, we have removed Reaction R2 from the main text. The correct reaction is described in Table S1 of the Supporting Information, as shown in R8-9.

$$OH + VOCs + O_2 \rightarrow RO_2 + products \quad \text{(R8)}$$

$$HCHO + OH + O_2 \rightarrow CO + H_2O + HO_2 \quad \text{(R9)}$$

4. **Comments:** *Line 66: O3 photolysis does not directly produce OH; it first generates O(1D), which subsequently reacts with water vapor to form OH. Therefore, please change "…by O3 photolysis at wavelengths below 320 nm (R6–R7) in the troposphere" to "…through O3 photolysis at wavelengths below 320 nm (R6–R7), followed by the reaction of O(1D) with water vapor in the troposphere.*

Reply: Thank you for your suggestion. We agree that O_3 photolysis does not directly produce OH radicals; instead, it first generates $O(^1D)$, which subsequently reacts with water vapor to form OH. In the revised manuscript, following the reviewer's earlier suggestions, we have removed Reaction R6-R7 from the main text. Furthermore, we have supplemented the detailed description of the calculation of OH radicals from O_3 photolysis in the Section 2.5.

"The RO_x budget is determined by the initial and termination reactions. The main sources of primary RO_x that initiate the RO_x cycle include the $O(^1D)$ channel of O_3 photolysis, and photolysis of HONO, HCHO, and other carbonyls, as well as the ozonolysis of alkenes (Zhou et al., 2024; Yang et al., 2021; Xue et al., 2016; Wang et al., 2017), shown as in R4-R7 in Table S1. The production rate of primary RO_x is calculated as Equation (4).

$$P(RO_x) = \varphi_{OH} j_{O(^1D)}[O_3] + j_{HONO}[HONO] + 2j_{HCHO-r}[HCHO] + \sum_i \left(\varphi^i_{OH} + \varphi^i_{HO_2} + \varphi^i_{RO_2}\right) k^i_{[alkene,O_3]} [alkene]^i [O_3] \quad (4)$$

$$\varphi_{OH} = 2 \cdot \frac{k_{[O(^1D),H_2O]}[H_2O]}{\left(k_{[O(^1D),O_2]}[O_2] + k_{[O(^1D),N_2]}[N_2] + k_{[O(^1D),H_2O]}[H_2O]\right)}$$

φ_{OH} in the first term for O_3 photolysis in Equation (4) is the yield of OH from the reaction of $O(^1D)$ with H_2O. φ^i_{OH}, $\varphi^i_{HO_2}$, and $\varphi^i_{RO_2}$ are the yields of OH, HO_2, and RO_2, respectively, generated in the ozonolysis reactions of each alkene species i with O_3." Line 255-262

5. **Comments:** *Lines 72-73: The statement that each complete ROx cycle converts two NO molecules to NO2 is too general. This stoichiometry applies only to an idealized propagation sequence involving successive RO2 + NO and HO2 + NO reactions, whereas actual VOC oxidation may follow competing pathways and produce different radical and ozone yields.*

Reply: Thank you for your suggestion. The statement is indeed too general. In the revised manuscript, following the reviewer's earlier suggestions, we have removed this statement.

6. **Comments:** *Lines 80-93 and Reaction R13: The description of high-NOx radical termination appears chemically inaccurate. Organic nitrates are generally formed through a branching channel of RO2 + NO, whereas reactions of RO2 with NO2 more commonly form peroxy nitrates or PAN-type*

reservoir species, depending on the RO2 structure. These products should not necessarily be treated as permanent radical termination because they can thermally decompose or otherwise recycle NOx and radicals. Please correct Reaction R13 and distinguish irreversible termination from temporary radical and NOx sequestration.

Reply: Thank you for your suggestion. The statement is indeed too general. In the revised manuscript, following the reviewer's earlier suggestions, we have removed this part. We agree that the original description was chemically inaccurate. Organic nitrate ($RONO_2$) formation occurs through a minor branching channel of the RO_2 + NO reaction, through RO_2 + NO_2. Reaction R13 in the manuscript has been corrected accordingly, as shown in Table S1 R16 of the revised manuscript. We also agree that RO_2 + NO_2 reactions generally form thermally peroxy nitrates or PAN-type reservoir species rather than permanent termination products. Given that our analysis centers on radical chain termination, we have removed the RO_2 + NO_2 pathway from the termination reactions and no longer treat it as a radical sink, without further discussion of the latter.

$$RO_2 + NO \rightarrow RONO_2 \qquad \text{(R16)}$$

7. **Comments:** *Lines 94-114: The discussion presents air-quality modeling primarily from the perspective of the chemical mechanism, making the model appear conceptually similar to a photochemical box model. Regional ozone simulations also depend strongly on emissions, meteorology, transport, mixing, deposition, boundary conditions, and spatial resolution. Please acknowledge these major sources of uncertainty and clarify that the chemical mechanism is one component of a broader modeling system. This context is important because the study aims to isolate mechanism-dependent differences.*

Reply: Thank you for your suggestion. We have added a discussion of the sources of uncertainty in simulations of ozone for regional air quality model and have cited relevant studies indicating that the gas-phase chemical mechanism is one of the main sources of this uncertainty. The specific additions are as follows:

"The accuracy of regional air quality model simulations of O_3 is influenced by emission inventories, meteorological inputs, grid resolution, boundary conditions and atmospheric chemical mechanisms (Gao and Zhou, 2024; Du et al., 2026). Among these factors, gas-phase chemical mechanism is one of main sources of the uncertainty (Gao and Zhou, 2024), which plays an important role in determine the chemical reactions rates governing O_3 formation and loss pathways (Yu et al., 2010)." Line 60-64

8. **Comments:** *Lines 97-98: The phrase 'O3 regional characteristics' is vague. Please clarify whether this refers to the spatial distribution, temporal variability, or regional formation processes of ozone.*

Reply: Thank you for your suggestion. we have revised this sentence accordingly in the revised manuscript. The specific changes are as follows:

"Given the limitations of field observations and laboratory experiments in capturing the regional-scale

spatial distributions, temporal variabilities, and the associated formation and transport processes of O_3, air quality models have become essential tools for quantitatively understanding O_3 formation mechanisms and evaluating emission control strategies." Line 56-59

9. **Comments:** *Lines 152: It is unclear what is meant by stating that ozone and its precursors 'accumulate and recycle' in the local atmosphere. While accumulation under stagnant basin conditions is understandable, 'recycle' could refer either to meteorological recirculation or to chemical recycling of reactive species. Please clarify the intended process.*

Reply: Thank you for your suggestion. We have revised this vague description, and the specific corrections are as follows:

"O_3 and its precursors in Chengdu are prone to accumulate and further intensify chemical recycling in the local atmosphere" Line 133-134

10. **Comments:** *Figure 1b: Showing only mean concentrations is not sufficient to characterize the NOx conditions at the two sites. Please consider adding error bars, such as standard deviation, or replacing the bars with box-and-whisker plots to show measurement variability and distributions. NO2 should also be typeset with a subscript in the panel.*

Reply: Thank you for your suggestion. We have replaced the bars with the box-and-whisker plots to show measurement variability and distributions. Moreover, NO_2 has been typeset with a subscript in the panel.

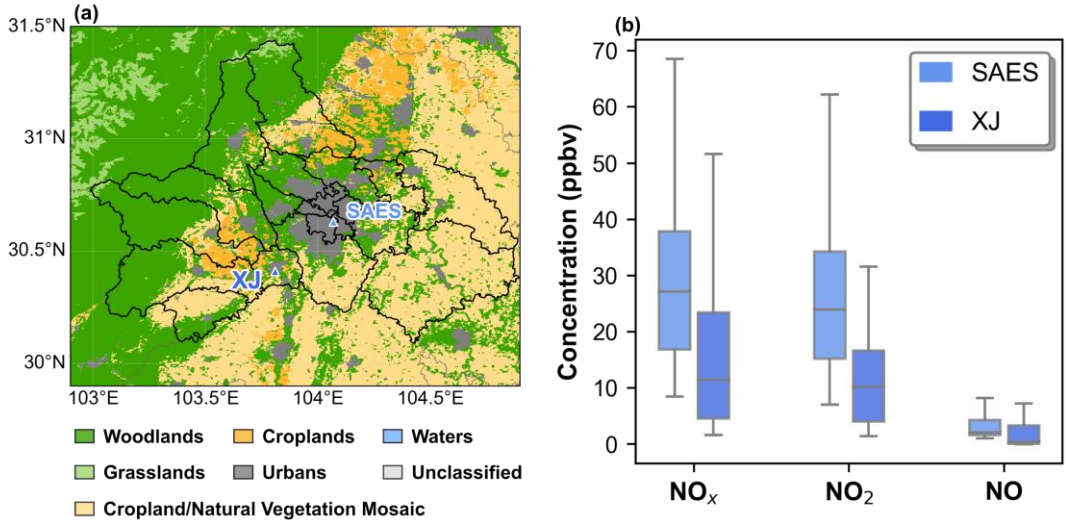


Figure 4 (a) Land use types in Chengdu and surrounding areas, along with the locations of the SAES site (light blue triangle) and XJ site (dark blue triangle). (b) Distribution of NO_x (NO_x = NO +NO_2), NO_2 and NO concentrations (ppbv) at the Sichuan Academy of Environmental Sciences (SAES) site and Xinjin (XJ) site during this pollution episode. The box plots present the 10th, 25th, 50th, 75th, and 90th percentiles of the statistical metrics individually.

11. **Comments:** *Lines 185-191: The manuscript lists the measured species, but except for OH and*

HO2, no information is provided on measurement techniques, detection limits, or measurement uncertainties/accuracies. Because these observations are used to evaluate model performance, this information should be provided, at least in the Supplement.

Reply: Thank you for your suggestion. We have added the details of instruments measuring trace gases in this revised manuscript.

"The trace gases include O_3, NO_x, nitrous acid (Smith et al., 2024), isoprene (ISOP), and nitric acid (HNO_3) at the urban site (SAES), and O_3, NO_x, HONO, ISOP, and formaldehyde (HCHO) at the suburban site (XJ). The details of instruments for measuring trace gases are summarized in Table S2." Line 170-172

Table S3 The details of instruments for measuring trace gases in this study.

Parameters	Method	Time resolution	Accuracy (%)	Limit of detection
O_3	UV absorption	1 min	± 5	0.5 ppbv
NO, NO_2	Chemiluminescence	1 min	± 20	0.5 ppbv 300 ppbv
VOC	GC–MS/FID[1]	1 h	± (15-20)	20–300 pptv
Formaldehyde	Hantzsch fluorimetry	1 min	±5	25 pptv
HNO_3	GAC-IC[2]	1 h	±5	0.13 μg/m³
HONO	Long-path absorption photometry	300 s	300 s ±20	10 pptv 10 pptv ±20%

Note. [1] GC–MS/FID is Gas Chromatography with Mass Spectrometry/with Flame Ionization Detection. [2] Gas and Aerosol Collector coupled with Ion Chromatography.

12. **Comments:** *Sections 2.1 and 2.2: Because meteorology strongly affects regional ozone through transport, mixing, temperature, and biogenic emissions, please provide standard meteorological performance metrics, including temperature, wind speed/direction, and humidity, at least in the Supplement.*

Reply: Thank you for your suggestion. We also have supplemented the observed meteorological parameters (temperature, relative humidity and wind speed) and evaluated of the performances of WRF in simulating these parameters, including error statistics (Table S9) and time-series plots comparing simulated and observation (Figure S3-5).

"Hourly meteorological parameters and trace gases were obtained. The meteorological parameters included wind speed at 10 m (WS10M), temperature at 2 m (T2M) and relative humidity (RH)." Line 167-169

"The WRF simulation was evaluated against meteorological observations of T2M, RH and WS10M at the SAES and XJ sites. The corresponding time series was shown in Figure S3-S5 and model performances were quantified using several statistical metrics, including correlation coefficient (R),

mean bias (MB), root-mean-square error (RMSE), and gross error (GE). The definitions and calculation formulas for these metrics are provided in Table S8, and the corresponding evaluation results are summarized in Table S9. The WRF simulation generally captured the observed variations in T2M and RH, with correlation coefficients ranging from 0.81 to 0.93. The RMSE for WS10M (1.4–1.6 m s^{-1}) were below the commonly benchmark of 2.0 m s^{-1} recommended by (Emery and Tai, 2001). Moreover, compared to previous studies (T2M: 2.8 ≤ RMSE ≤ 3.3 K; RH: 14.3% ≤ RMSE ≤ 16.2% and 11.0% ≤ GE ≤ 12.6%; WS10M: 0.5 m s^{-1} ≤ MB ≤ 1.1 m s^{-1} and 1.8 m s^{-1} ≤ RMSE ≤ 2.3 m s^{-1}) over SCB in summer (Qiao et al., 2019), the statistical indices of T2M (2.2 K ≤ GE ≤ 3.1 K), RH (10.6% ≤ RMSE ≤ 12.6% and 8.1% ≤ GE ≤ 10.3%) and WS10M (-0.3 m s^{-1} ≤ MB ≤ 0.9 m s^{-1} and 1.4 m s^{-1} ≤ RMSE ≤ 1.6 m s^{-1}) in this study was closer to observation. Overall, the simulated meteorological fields provided a reasonable basis for the subsequent CMAQ simulations." Line 207-220

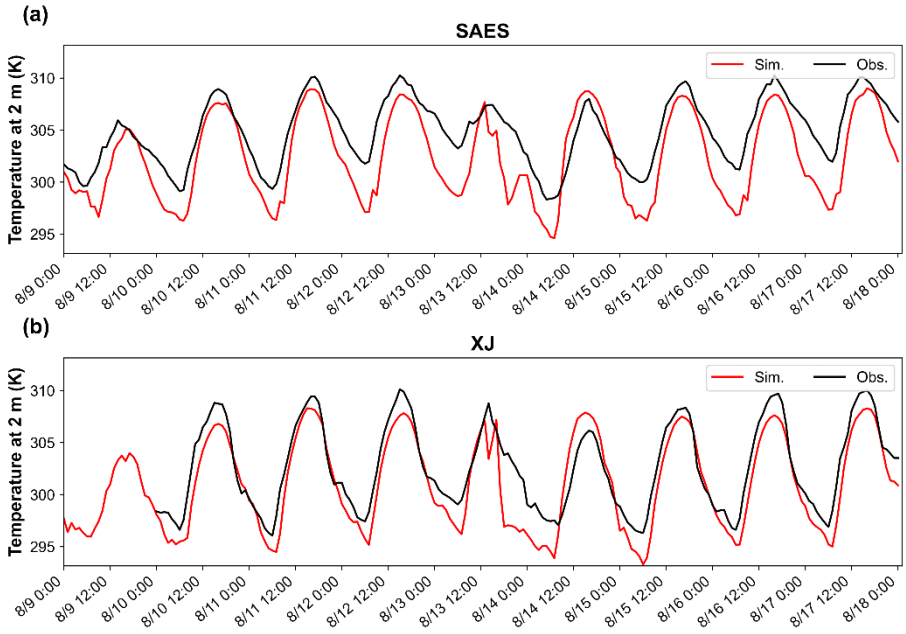


Figure S3 Time series of temperature (K) at 2 m simulation (red lines) and observation (black lines) at SEAS (a) and XJ (b) sites.

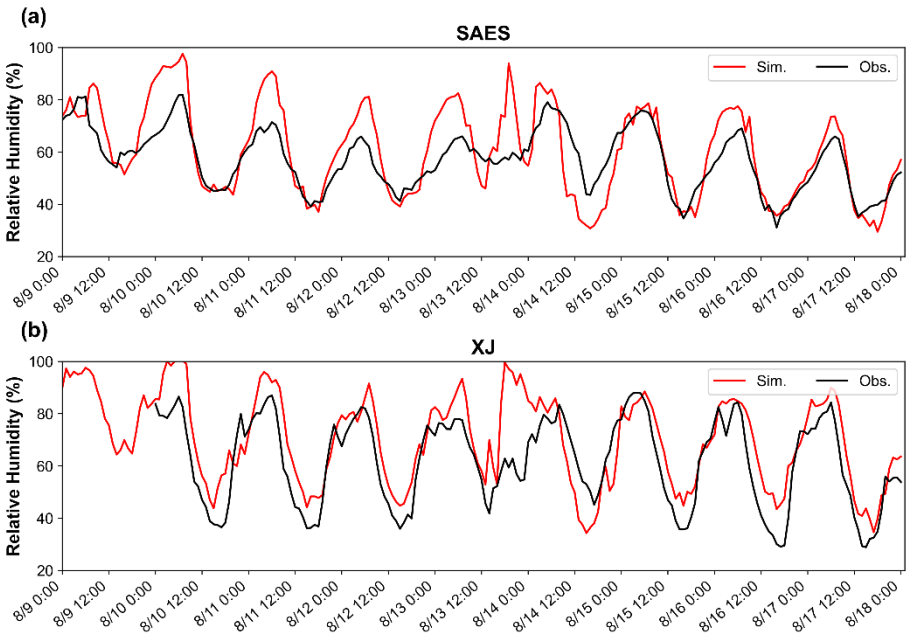


Figure S4 Time series of relative humidity (%) simulation (red lines) and observation (black lines) at SEAS (a) and XJ (b) sites.

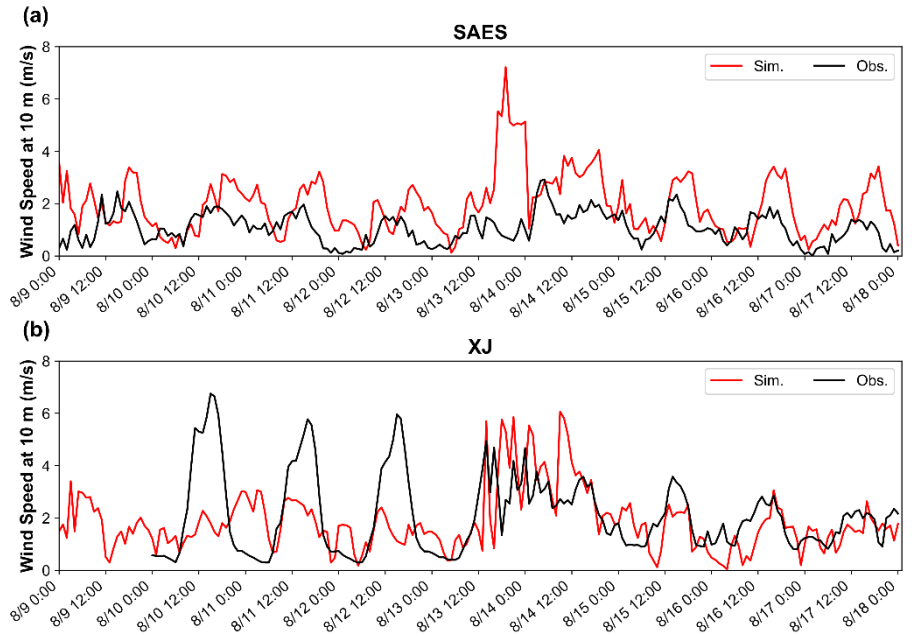


Figure S5 Time series of wind speed (m/s) at 10 m simulation (red lines) and observation (black lines) at SEAS (a) and XJ (b) sites.

Table S8 Statistical metrics for photochemical mechanisms performance evaluation discussed in this study.

Statistic/abbreviation	Definition	Notes

Correlation coefficient (R)	$\frac{\sum[(S_i-\bar{S})\times(O_i-\bar{O})]}{\sqrt{\sum(S_i-\bar{S})^2\times\sum(O_i-\bar{O})^2}}$	-1≤R≤1
Index of Agreement (IOA)	$1-\frac{\sum(S_i-O_i)^2}{\sum(\lvert S_i-\bar{O}\rvert+\lvert O_i-\bar{O}\rvert)^2}$	0≤IOA≤1
Mean Fractional Bias (MFB)	$\frac{2}{N}\sum\frac{(S_i-O_i)}{(S_i+O_i)}\times 100$	-200%≤MFB≤+200%
Mean Fractional Error (MFE)	$\frac{2}{N}\sum\frac{\lvert S_i-O_i\rvert}{(S_i+O_i)}\times 100$	0≤MFE≤+200%
Root Mean Square Error (RMSE)	$\frac{\sqrt{\frac{1}{N}\sum(S_i-O_{i)}{}^2}}{\sqrt{\frac{1}{N}\sum[(S_i-\bar{S})-(O_i-\bar{O})]^2}}$	/
Gross Error (GE)	$\frac{2}{N}\sum\lvert S_i-O_i\rvert$	/

Note. Subscript i represents the pairing of N observations O and simulations S by site and time. Overbars signify means over site and/or time.

Table S9 The WRF model performance for temperature (°C) at 2 m, relative humidity (%) at 2 m, wind speed (m/s) at SAES and XJ site.

	Obs.	**Sim.**	**R**	**MB**	**RMSE**	**GE**
2-m Temperature (K)						
SAES	302.4	304.8	0.9	-2.4	3.1	2.7
XJ	301.0	302.7	0.93	-1.5	2.2	1.8
2-m Relative Humidity (%)						
SAES	60.7	57.0	0.84	3.7	10.6	8.1
XJ	70.5	61.7	0.81	7.2	12.6	10.3
10-m Wind Speed (m/s)						
SAES	2.0	1.1	0.32	0.9	1.4	1.0
XJ	1.9	2.1	0.32	-0.3	1.6	1.2

Note. R is correlation coefficient; MB is mean bias; RMSE is root mean square error; GE is gross error. The equations of R, MB, RMSE and GE can be found in Table S8.

13. **Comments:** *Lines 196-211: The three simulations use different CMAQ chemical configurations, including different aerosol modules (AE7/AE7i versus AE6), in addition to different gas-phase mechanisms. Please clarify to what extent the reported inter-mechanistic differences can be attributed specifically to gas-phase chemistry rather than to differences in the accompanying model configurations.*

Reply: Thank you for your suggestion. Kulkarni et al. (2021) previously reported that different aerosol module versions (AERO6 and AERO7) in the CMAQ model have little impact on ozone simulations

over the United States, with the results showing that the two versions have a negligible effect on MDA8 O_3 over inland areas, while only slight differences were observed along the coastal regions (shown as Response Figure 2). Since the Sichuan Basin targeted in our study is an inland region, it can be inferred that the influence of AERO6 and AERO7 on ozone simulations over this basin is likewise negligible.

Furthermore, compared to AERO7, AERO7i only provides more the diagnostic information in terms of IEPOX SOA identity, as well as some minor additional high-NOx pathways to SOA (a particle-phase isoprene dinitrate and does not materially affect the simulation results (Appel et al., 2021). Therefore, the effects of different aerosol module versions (AERO6, AERO7, and AERO7i) on ozone simulations in this study can be negligible.

14. **Comments:** *Section 2.2: The manuscript provides considerable detail on VOC mapping but very limited information on how the chemical mechanisms themselves differ. Please provide a systematic comparison of the three mechanisms, including differences in reaction-rate coefficients and whether important pathways such as chlorine chemistry, RO2 chemistry, and intramolecular isomerization are represented.*

Reply: Thank you for your suggestion. We agree that the three mechanisms differ in several aspects of their chemical formulations. However, a comprehensive reaction-by-reaction comparison of CB06, SAPRC07, and RACM2, including all reaction-rate coefficients and individual chemical pathways, is beyond the scope of the present study. The principal structural differences among the three mechanisms have already been introduced in the Introduction, particularly their different VOC lumping, which represent one of the major distinctions among CB06, SAPRC07, and RACM2. These differences directly affect the representation of VOC oxidation, intermediate products, and subsequent RO_2 chemistry. We note that the objective of this study is not to provide a comprehensive intercomparison of the chemical structures of the three mechanisms, but rather to investigate how their different chemical representations affect simulated O_3 and RO_x chemistry under contrasting-NOx atmospheric conditions. Therefore, instead of exhaustively comparing individual reaction-rate coefficients, our analysis focuses on the key chemical processes that directly contribute to the simulated differences, including O_3 formation and loss pathways, RO_x primary production, radical propagation, and radical termination. These process-level differences are quantitatively evaluated in Sections 3.

15. **Comments:** *Section 2.3: Please provide a quantitative evaluation of the customized RACM2 emission mapping. For example, how well are total VOC emissions, carbon mass, and VOC reactivity conserved relative to the original inventory? This is important because the customized inventory is central to the inter-mechanism comparison.*

Reply: Thank you for your suggestion. We agree that the consistency of the customized RACM2 emission mapping should be more clearly demonstrated because the RACM2 emissions were generated through mechanism-specific mapping of the original VOC inventory.

First, we have expanded Section 2.3 and Table S5-7 to provide a more detailed comparison of the

primary VOC emission species used in CB06, SAPRC07, and RACM2, together with their corresponding mapping relationships. All three mechanism-specific emission inputs were derived from the same underlying VOC inventory. The RACM2 inventory was therefore not constructed from an independent emission dataset, but was generated by mapping the original VOC species into the corresponding RACM2 surrogate species according to their chemical characteristics. The revised table makes the consistency of the primary VOC inputs among the three mechanisms more transparent.

In addition, we examined the overall VOC oxidation reactivity represented by the three mechanisms. The integrated reaction rates of OH with major VOC classes were generally comparable among CB06, SAPRC07, and RACM2, with particularly similar total OH + VOC reaction rates between RACM2 and SAPRC07 (Fig 9). Because OH-initiated oxidation represents a major sink of VOCs and controls subsequent RO_2 formation, the comparable OH + VOC reaction rates provide a chemical consistency check indicating that the customized RACM2 mapping does not introduce an anomalously high or low overall VOC reactivity.

At the broader photochemical level, RACM2 and SAPRC07 produced comparable O_3 concentrations and broadly consistent RO_x primary production and termination rates. Although these similarities do not directly demonstrate conservation of VOC emissions or carbon mass, as the modeled chemical budgets are also influenced by mechanism-specific kinetics and reaction pathways, they provide additional system-level evidence that the customized RACM2 emission mapping does not introduce a substantial artificial bias into the simulated photochemical system.

16. **Comments:** *Figure 2 and Lines 250-254: Please mark XJ in Figure 2. The simulation period is also inconsistent between the Figure 2 caption (August 9-18) and the text (August 9-19). Please clarify and use a consistent period throughout.*

Reply: Thank you for your suggestion. Regarding the simulation period, we have checked the descriptions and confirm that all simulations consistently cover the period (August 9-18).

17. **Comments:** *Figure 3: Please clarify which monitoring sites were included in the statistical analysis and whether XJ is included. If the statistics combine urban and suburban sites, the results should be separated by site type because the preceding discussion shows substantially different model performance between these environments. Please also use a consistent evaluation framework for Figures 3 and 4, or explain why Figure 4 separates urban and suburban sites and uses daytime data whereas Figure 3 does not.*

Reply: Thank you for your suggestion. The statistics in the manuscript indeed combined urban and suburban sites. Following your suggestion, we have revised the manuscript to present the statistical comparisons between simulated and observed ozone separately for urban and suburban sites, and Figure 3 has been updated accordingly. In addition, we have added site-category labels (urban/suburban) in the table of sites location information (Table S3) and supplemented the statistical analysis in the main text for updated Figure 3.

Regarding the use of only daytime data in Figure 4, our main purpose was to more clearly reflect the

influence of different chemical mechanisms on the simulation of ozone precursors. During the daytime, the chemical production and removal of ozone precursors are primarily governed by photochemical reactions involving OH radicals, and the differences among chemical mechanisms are also mainly manifested in their descriptions of photochemical processes. Nighttime chemistry, however, is distinctly different: processes such as NO_3 radical oxidation and heterogeneous reactions can significantly affect precursor concentrations, and these processes are subject to relatively high parametric uncertainties in the models. If nighttime data were also included, the effects of nighttime processes that are not directly related to the chemical mechanisms under discussion could be introduced, thereby interfering with the evaluation of the ability of different mechanisms to simulate ozone precursors. Therefore, Figure 4 focuses on daytime data, which can more reasonably reflect the performance of different chemical mechanisms in simulating ozone precursors during photochemically dominated periods.

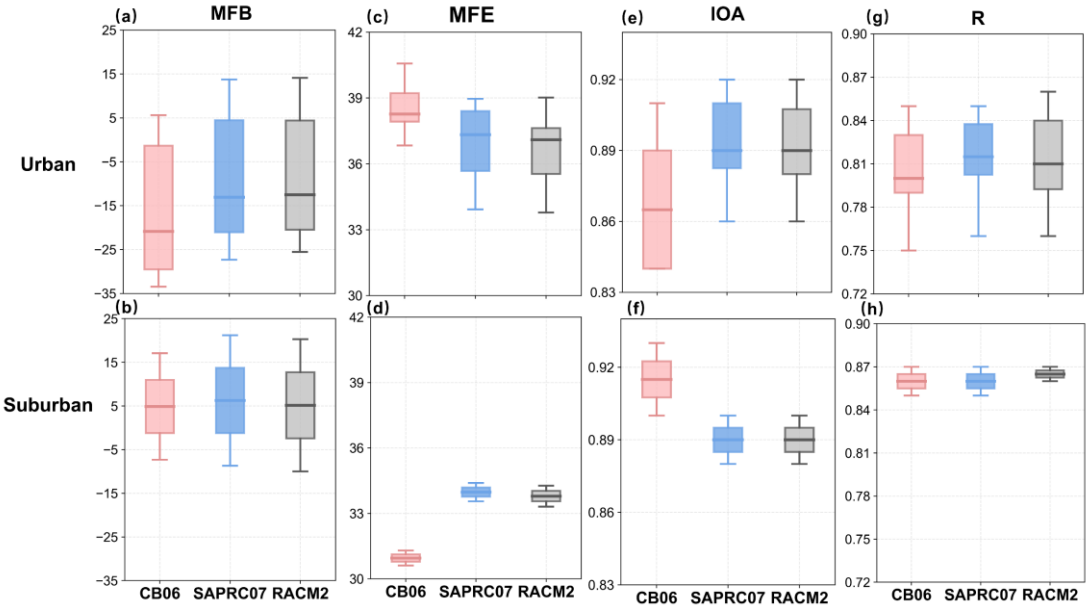


Figure 5 Statistical analysis of hourly O_3 simulated by three photochemical mechanisms (CB06, SAPRC07 and RACM2) s at urban sites and suburban sites across Chengdu region during August 9-August 18, 2019. The box plots present the 10th, 25th, 50th, 75th, and 90th percentiles of the statistical metrics individually. The statistical metrics, including mean fractional bias (MFB), mean fractional error (MFE), index of agreement (IOA) and correlation coefficient (R), are presented. MFB and MFE are given as percentages. The unit of MFB and MFE is percent (%).

Table S3 Location information of the China National Environmental Monitoring stations in Chengdu and in-situ field sites.

Type	Station ID	Station Name	Longitude	Latitude	Urban/Suburban Category
China National Environmental	1431A	JinQuanLiangHe	103.97275°E	30.72358333°N	Urban
	1432A	ShiLiDian	104.176°E	30.6872°N	Urban
	1433A	SanWaYao	104.079°E	30.5706°N	Urban

Monitoring stations	1434A	ShaHePu	104.1113889°E	30.63°N	Urban
	1437A	JunPingJie	104.054°E	30.6578°N	Urban
	2880A	DaShiXiLu	104.0238889°E	30.65638889°N	Urban
	3136A	LongQuanYiQuQuZhengFu	104.2725°E	30.5589°N	Urban
in-situ field sites	/	Xinjin (XJ)	103.81°E	30.41°N	Suburban
	/	Sichuan Academy of Environmental Sciences (SAES)	104.07°E	30.63°N	Urban
	/	Guanghan	104.21°E	31.03°N	Suburban
	/	Chengdu University of Information Technology	103.99°E	30.58°N	Urban
	/	Chengdu Academy of Environmental Sciences	104.05°E	30.65°N	Urban

18. **Comments:** *Lines 281-283: The attribution of lower ozone in CB06 to insufficient NO2 recycling from nitrates appears too definitive. This explanation is cited from a previous study but is not demonstrated here, and the manuscript later shows that NO2 is generally overestimated by all three mechanisms. Please provide evidence from the present simulations or soften the interpretation.*

Reply: Thank you for your suggestion. Under the condition of overestimated NO_2 concentrations, it was indeed inappropriate to cite the literature attributing the lower ozone in CB06 to "insufficient NO_2 recycling from nitrates." Accordingly, we have removed this explanation from the revised manuscript.

19. **Comments:** *Lines 317-320: RACM2 shows the closest agreement with observed HONO, but the origin of this inter-mechanistic difference is not discussed. Because HONO photolysis is subsequently identified as an important ROx source, please explain which HONO-related reactions, sources, or precursor treatments differ among the mechanisms and lead to the higher HONO simulated by RACM2.*

Reply: Thank you for your suggestion. HONO photolysis is indeed one of the important primary sources of RO_x. However, in this study, the analysis of HONO sources and sinks falls outside the primary scope of this study and is therefore not conducted.

20. **Comments:** *Lines 322-329: The phrase 'uncertainties in ISOP-related oxidation chemistry' is too vague. Clarify whether this refers to differences in direct chemical loss of isoprene or to downstream isoprene oxidation chemistry that alters radical recycling and OH. This distinction is important because Figure 5 shows substantial inter-mechanistic differences in OH, which could directly affect simulated ISOP lifetime and concentration.*

Reply: Thank you for your suggestion. We agree that the original wording was vague. However, differences among mechanisms in simulated isoprene and OH concentrations alone are not sufficient to determine whether the uncertainty arises from direct chemical loss of isoprene or from downstream isoprene oxidation chemistry that alters radical recycling and OH. In this study, our main focus is the

inter-mechanistic differences in ozone production; we therefore do not discuss the isoprene-related differences in further detail.

21. **Comments:** *Lines 330-335: The HNO_3 overestimation is attributed mainly to overestimated NO2. However, HNO3 production through OH + NO2 depends on both reactants, and Figure 5 shows that OH is also substantially overestimated, particularly by RACM2, which also shows the largest HNO3 bias. Please discuss the contribution of OH overestimation to excessive HNO3 production. Furthermore, HNO3 concentrations are strongly affected by partitioning to particulate inorganic nitrate and other loss processes. Given that different aerosol modules are used for the three mechanisms, please explicitly examine and discuss HNO3-inorganic nitrate partitioning before attributing the differences primarily to gas-phase chemistry.*

Reply: Thank you for your suggestion. We would first like to clarify that the original manuscript did not intend to attribute the HNO_3 overestimation primarily or exclusively to the overestimation of NO_2. The original statement was that "the overestimations are likely attributed to the previously noted overestimation of NO_2 concentrations, which enhances the OH + NO_2 reaction and subsequently accelerates the production of HNO_3." We agree, however, that this explanation was incomplete because HNO_3 production through OH + NO_2 depends on both reactants.

As shown in Fig. 5, OH concentrations are also overestimated, particularly in RACM2, which exhibits the largest positive HNO_3 bias. Therefore, the simultaneous overestimation of both OH and NO_2 can enhance the OH + NO_2 reaction rate and contribute to excessive gas-phase HNO_3 production. We have supplemented the corresponding discussion to explicitly acknowledge the contribution of OH overestimation rather than attributing the HNO_3 bias solely to NO_2.

"This OH overestimation may enhance the OH + NO_2 reaction and thereby contribute to excessive HNO_3 production, particularly in RACM2, which also showed the largest positive HNO_3 bias (Fig. 4e)" Line 441-443

We also agree that simulated HNO_3 concentrations are affected not only by gas-phase production but also by gas–particle partitioning with particulate nitrate and by subsequent loss processes. In the present simulations, however, the major factors controlling thermodynamic HNO_3–NO_3^- partitioning were treated consistently among the same configurations. All simulations were driven by the same offline WRF meteorological fields and therefore used identical temperature and relative humidity conditions. In addition, the aerosol thermodynamic equilibrium calculations in the different CMAQ configurations were based on ISORROPIA II, and the NH_3 emission inputs were identical among the simulations. These common settings substantially constrain differences in the thermodynamic partitioning environment. Therefore, we consider differences in aerosol-module configuration unlikely to be the dominant factor responsible for the inter-mechanistic differences in HNO_3.

22. **Comments:** *Lines 343-345: This statement is unclear and appears inconsistent with the following results. Figure 4 does not show temporal HCHO peaks, so the meaning of the 'superior performance of SAPRC07 in simulating HCHO peaks' is unclear. In addition, Figure 5 shows that RACM2 produces*

the highest OH while SAPRC07 produces the highest HO_2, so the general statement that SAPRC07 has higher radical concentrations is inaccurate. Please clarify the radical species, provide the appropriate figure or section reference, and explain the mechanistic basis for linking the HCHO bias to radical concentrations.

Reply: Thank you for your suggestion. We agree that the original statement was not sufficiently precise and could lead to confusion. We have therefore revised the corresponding text.

"SAPRC07 produced the highest daytime HO_2 peaks at the XJ site, corresponding to the simulated highest mean HO_2 concentration (10×10^8 molecules cm^{-3}), followed by CB06 (9.4×10^8 molecules cm^{-3}) and RACM2 (9.1×10^8 molecules cm^{-3}). This feature coincided with the higher simulated-to-observed HCHO ratio for SAPRC07 (Fig. 4j). Because HCHO photolysis is one of important primary sources of HO_2 radicals, the enhanced HCHO abundance in SAPRC07 may partly contribute to its higher simulated HO_2 concentrations." Line 444-449

23. **Comments:** *Figure 5: Please clearly indicate which panels correspond to CB06, SAPRC07, and RACM2, respectively, and mark XJ on the maps.*

Reply: Thank you for your suggestion. We have now added clear labels indicating which panels correspond to CB06, SAPRC07, and RACM2, respectively, and have marked the XJ site on the maps in Figure 5.

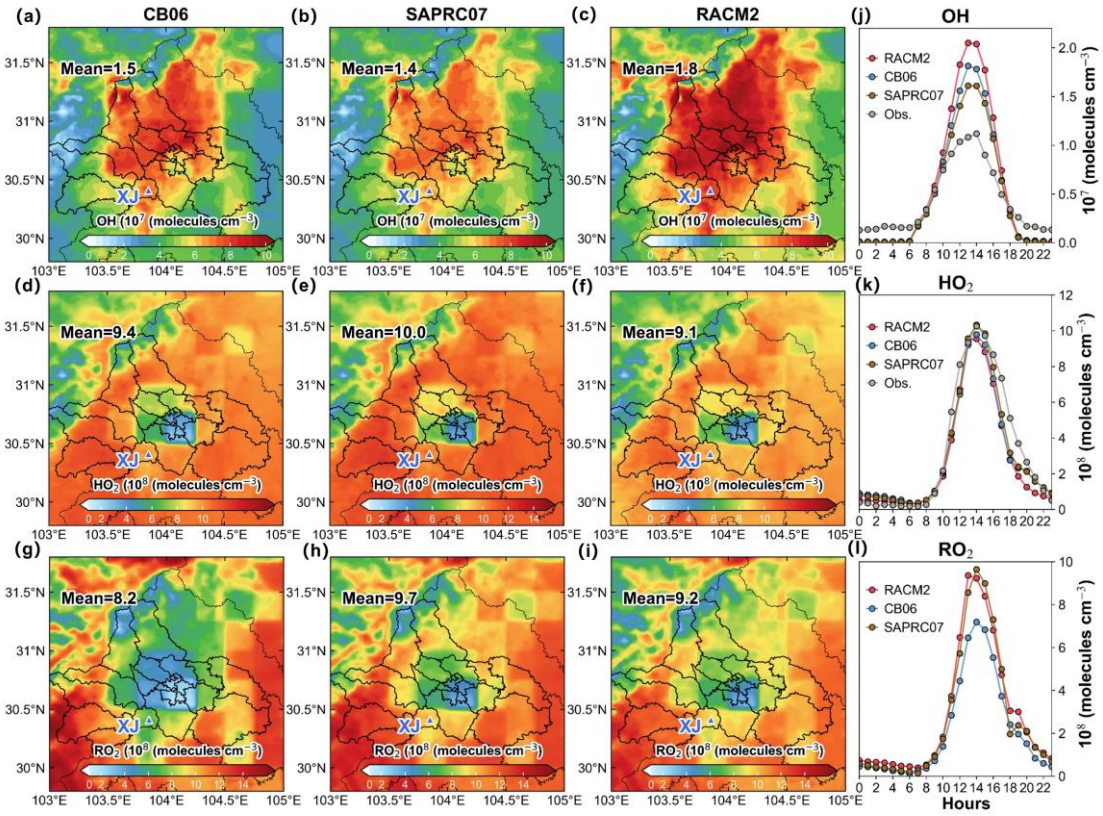


Figure 5 Regional distributions of OH, HO_2 and RO_2 concentration at 14:00 local time and diurnal variation at XJ site of OH, HO_2 and RO_2 concentration simulated by three photochemical mechanisms during August 9-August 18, 2019. The location of XJ site is marked with a dark blue triangle.

24. **Comments:** *Line 358: The statement that the spatial distributions are 'largely consistent' is too qualitative. Please quantify the degree of agreement or specify the range of inter-mechanistic differences.*

Reply: Thank you for your suggestion. Here, "largely consistent" was intended to describe the similarity in the spatial distribution patterns of OH, HO_2, and RO_2 radicals among the three chemical mechanisms. Specifically, the three mechanisms generally reproduced similar locations of high- and low-concentration regions across Chengdu. We have therefore revised the text to explicitly describe these common spatial features and supplemented the discussion with the regional mean concentrations to quantitatively characterize the inter-mechanistic differences.

"Generally, the three chemical mechanisms generally exhibited similar spatial distribution patterns for OH, HO_2, and RO_2 radicals, with comparable locations of high- and low-concentration regions across Chengdu (Fig. 5)." Line 419-421

"For OH, the RACM2 simulated a regional mean concentration of 1.8×10^7 molecules cm^{-3}, notably higher than those simulated by SAPRC07 (1.4×10^7 molecules cm^{-3}) and CB06 (1.5×10^7 molecules cm^{-3})." Line 433-435

"In contrast the OH behaviors, SAPRC07 produced the highest daytime HO_2 peaks at the XJ site, corresponding to the simulated highest mean HO_2 concentration (10×10^8 molecules cm^{-3}), followed by CB06 (9.4×10^8 molecules cm^{-3}) and RACM2 (9.1×10^8 molecules cm^{-3})." Line 443-446

"For RO_2 radicals, the CB06 mechanism yielded a regional mean RO_2 concentration of 8.2×10^8 molecules cm^{-3}, markedly lower than the 9.2×10^8 and 9.7×10^8 molecules cm^{-3} simulated by RACM2 and SAPRC07, respectively—a gap of approximately 11%~16%." Line 449-451

25. **Comments:** *Lines 363-365: The explanation of low urban OH focuses only on OH + NO2. Reactions of OH with VOCs, particularly anthropogenic VOCs in the urban core, may also represent an important OH sink and should be mentioned.*

Reply: Thank you for your suggestion. OH + VOC reactions generally initiate or propagate the RO_x radical chain by converting OH into RO_2 radicals, as illustrated by the reactions summarized in Table S1, rather than leading to a net loss of the RO_x radicals. In contrast, reactions between OH radical and NO_x, particularly $OH + NO_2 \rightarrow HNO_3$, are generally regarded as important radical termination pathways under high-NO_x conditions and thus result in a net removal of RO_x radicals. Therefore, we retain the emphasis on the $OH + NO_2$ pathway in the manuscript.

26. **Comments:** *Lines 383-387: The conclusion that lower RO2 in CB06 explains its lower ozone is incomplete without discussing the origin of the RO2 difference. Please relate this to mechanism-specific VOC lumping and speciation (Table S3), which can alter OH reaction rates, RO2 yields and identities, and subsequent propagation chemistry. A bulk RO2 comparison alone is insufficient to explain the inter-mechanistic difference in ozone.*

Reply: Thank you for your suggestion. We agree that the simulated RO_2 differences can ultimately be related to mechanism-specific VOC lumping and speciation, which may influence VOC oxidation, RO_2

formation, and subsequent propagation chemistry. However, in this study we focused on the differences of simulated O_3 production and corresponding mechanisms among the three gas-phase chemicals mechanisms. Therefore, we do not further discuss the contributions of individual RO_2 species and their specific reaction rates in detail here.

Because reactions of both HO_2 and RO_2 radicals with NO constitute the chemical pathways for O_3 production, as expressed in Eq. (1), the relatively similar HO_2 levels suggest that the inter-mechanistic differences in O_3 production are more likely associated with differences in RO_2 radicals. We have revised the expressions.

"Moreover, the relatively similar simulated HO_2 levels and the substantially larger inter-mechanistic differences in RO_2 suggest that the differences in O_3 formation may be largely related to variations in simulated RO_2 abundance rather than HO_2." Line 454-456

27. **Comments:** *Lines 393-410: The discussion is largely descriptive and does not explain the origin of the different P(O3) among the three mechanisms. Please relate these differences to mechanism-specific VOC lumping/speciation (Table S3), VOC reactivity, and subsequent RO2 chemistry. For example, the apparently larger role of alkene-related chemistry in RACM2, particularly at the urban site, warrants further discussion.*

Reply: Thank you for your suggestion. We have revised the discussion to better explain the origin of the inter-mechanistic differences in $P(O_3)$. Our revised analysis shows that the differences in gross O_3 formation are mainly associated with the RO_2 + NO pathway, particularly at the urban site. The RO_2 + NO reaction rates were 22.0, 19.5, and 17.8 ppbv h^{-1} for RACM2, SAPRC07, and CB06, respectively, consistent with the larger inter-mechanistic differences in simulated RO_2 concentrations (Fig. 5). This suggests that mechanism-specific VOC representation and subsequent RO_2 chemistry are important contributors to the differences in $P(O_3)$, especially under high-NO_x conditions.

We also expanded the discussion of alkene chemistry. RACM2 showed a larger O_3 + alkene reaction rate at the urban site (1.2 ppbv h^{-1}) than SAPRC07 and CB06 (both 0.8 ppbv h^{-1}). This likely reflects differences in alkene lumping and reactivity among the mechanisms, which can affect both direct O_3 loss and subsequent RO_x chemistry. To further examine this difference, we compared the O_3 reaction rate constants of the major alkene species represented in the three mechanisms at 298 K (Response Fig. 3). The rate constants for ethene, isoprene, and the less reactive alkene groups are generally comparable among the three mechanisms. In contrast, the more reactive internal-alkene group in RACM2 (OLI, 2.58×10^{-16} cm^3 $molecule^{-1}$ s^{-1}) has a higher O_3 reaction rate constant at 298 K than the corresponding highly reactive alkene groups in SAPRC07 (OLE2, 1.27×10^{-16} cm^3 $molecule^{-1}$ s^{-1}) and CB06 (IOLE, 1.57×10^{-16} cm^3 $molecule^{-1}$ s^{-1}). This difference, together with mechanism-dependent alkene lumping and simulated alkene concentrations, may contribute to the stronger O_3 + alkene chemistry in RACM2. These results have been incorporated into the revised manuscript.

"Differences in O_3 + Alkenes were also apparent, especially at the urban site, where the corresponding rates for RACM2, SAPRC07, and CB06 were 1.2, 0.8, and 0.8 ppbv h^{-1}, respectively. These differences likely reflect the mechanism-dependent representation of alkene species and their reactivities toward

O_3. For example, the more reactive internal-alkene group in RACM2 (OLI, 2.58×10^{-16} cm^3 molecule^{-1} s^{-1}) has a higher O_3 reaction rate constant at 298 K than the corresponding highly reactive alkene groups in SAPRC07 (OLE2, 1.27×10^{-16} cm^3 molecule^{-1} s^{-1}) and CB06 (IOLE, 1.57×10^{-16} cm^3 molecule^{-1} s^{-1}).” Line 491-497

Response Table 1. Rate constants for the reactions of O_3 with major alkene species represented in SAPRC07, CB06, and RACM2 at 298 K.

Mechanism	Alkenes Species	k_{O_3} at 298 K (cm^3 molecule^{-1} s^{-1})
SAPRC07	ETHENE	1.59×10^{-18}
SAPRC07	ISOPRENE	1.29×10^{-17}
SAPRC07	OLE1	1.06×10^{-17}
SAPRC07	OLE2	1.27×10^{-16}
CB06	ETH	1.58×10^{-18}
CB06	ISOP	1.27×10^{-17}
CB06	OLE	1.00×10^{-17}
CB06	IOLE	1.57×10^{-16}
RACM2	ETE	1.59×10^{-18}
RACM2	ISO	1.28×10^{-17}
RACM2	OLT	1.03×10^{-17}
RACM2	OLI	2.58×10^{-16}

28. **Comments:** *Line 417: The description of NOx-ROx interactions as continuously 'generating' HO2 and RO2 is potentially misleading. Please distinguish radical propagation/recycling from the primary ROx production pathways.*

Reply: Thank you for your suggestion. We have revised the expressions.

“The coupling between the NO_x and RO_x cycles promotes radical propagation and recycling, facilitating the conversion of NO to NO_2 and net photochemical O_3 production.” Line 522-523

29. **Comments:** *Lines 422-425: RACM2 is reported to produce the highest P(ROx), particularly under urban high-NOx conditions, but the chemical origin of this difference is not discussed. Please identify which source pathways or mechanism-specific treatments are primarily responsible. The statements of 'considerable divergence' under urban conditions and 'more consistent results' under suburban conditions should also be supported with corresponding P(ROx) values or inter-mechanistic differences.*

Reply: Thank you for your suggestion. We have revised the manuscript to provide quantitative support for the inter-mechanistic differences in $P(RO_x)$ and to clarify the dominant source pathways for the differences. The results indicated that the largest inter-mechanistic difference at the urban site for $P(RO_x)$ occurred in the photolysis of carbonyl compounds, with production rates of 2.1, 1.6, and 1.4 ppbv h^{-1} for RACM2, SAPRC07, and CB06, respectively. This stronger carbonyl-photolysis source is therefore an important contributor to the higher $P(RO_x)$ simulated by RACM2 under urban high-NO_x conditions. At the suburban site, the major RO_x source pathways were more comparable among the three mechanisms, consistent with the smaller differences in total $P(RO_x)$. The corresponding discussion and quantitative pathway information have now been added to the revised manuscript.

30. **Comments:** *Lines 427-440: This paragraph primarily lists the contributions shown in Figure 7 without providing further interpretation. Please focus on mechanistically meaningful differences among the three mechanisms and explain why the ROx source distributions become more similar under suburban low-NOx conditions.*

Reply: Thank you for your suggestion. We have revised this section to focus on the mechanistically meaningful differences in primary RO_x radical sources among the three mechanisms. At the urban site, the largest inter-mechanistic difference occurred in the photolysis of carbonyl compounds. This indicates that differences in the representation and photochemistry of carbonyl species are an important source of the higher $P(RO_x)$ in RACM2 under high-NO_x urban conditions. Under suburban low-NO_x conditions, the dominant RO_x primary source shifted toward O_3 photolysis, which contributed 38.2%–40.5% and showed little variation among the three mechanisms. Meanwhile, the relative importance of more mechanism-sensitive pathways, particularly carbonyl photolysis and O_3 + alkenes, decreased. Consequently, the influence of mechanism-specific VOC and carbonyl chemistry on the overall RO_x source distribution was reduced, leading to more similar $P(RO_x)$ source distributions among the three mechanisms at the suburban site.

31. **Comments:** *Lines 434-436: The explanation that the higher other-carbonyl photolysis contribution in RACM2 may result from differences in photolysis parameters is not supportive. The manuscript does not describe how the relevant photolysis parameters differ among CB06, SAPRC07, and RACM2. Please identify the specific parameterizations, such as absorption cross-sections, quantum yields, or photolysis frequencies, and provide evidence that they explain the higher contribution in RACM2. Differences in carbonyl concentrations and speciation due to different VOC lumping methods should also be considered.*

Reply: Thank you for your suggestion. We agree that the previous explanation lacked sufficient supporting evidence and may have been overly speculative. Therefore, we have removed the corresponding description from the revised manuscript.

32. **Comments:** *Lines 450-451: This statement is misleading because OH + NO2 remains the dominant ROx termination pathway at the suburban site, contributing nearly 50% of total loss. Please*

revise the text to state that HO2 + RO2, HO2 + HO2, and RO2 + RO2 become relatively more important under suburban low-NOx conditions. Please also provide their quantitative contributions, as done for HNO3 and RONO2.

Reply: Thank you for your suggestion. We have revised the corresponding text in the manuscript accordingly.

"At the high-NO_x urban site, RO_x termination was mainly driven by OH+NO_2 to form HNO_3 (64.8% ~ 66.3%), followed by $RONO_2$ formation (16.9% ~ 24.4%)." Line 566-567

"In contrast, the RO_x termination became more distributed across multiple pathways at the suburban site. Although OH + NO_2 remained the largest individual RO_x radical loss pathway, its contribution decreased to 47.0%–50.8%." Line 574-576

"Meanwhile, the relative contributions of peroxy-radical termination pathways increased, including HO_2 + RO_2 (13.8%–20.6%), HO_2 + HO_2 (10.5%–13.4%), and RO_2 + RO_2 (7.8%–10.7%)." Line 578-579

33. **Comments:** *Lines 459-467: The manuscript uses the H2O2/HNO3 ratio to infer VOC-limited and NOx-limited regimes, but no diagnostic threshold or criterion is provided. Please specify the threshold values used to distinguish the regimes and provide an appropriate reference or justification for their application here.*

Reply: Thank you for your suggestion. We have revised the manuscript to provide a clearer description of the H_2O_2/HNO_3 ratio indicator, including the diagnostic criteria and threshold values used to distinguish VOC-limited and NO_x-limited regimes, together with the corresponding references and justification for their application in this study.

"Therefore, the ratios of major products or its production rates from termination reactions, such as H_2O_2/HNO_3, can provide a useful indicator of the prevailing radical-termination regime and the associated NO_x chemical environment. Previous studies examined that the H_2O_2/HNO_3 can be used as a robust indicator for determining O_3 formation regimes (Wei et al., 2018; Liu et al., 2010; Cordiner et al., 2002). The classic threshold of H_2O_2/HNO_3 separating the O_3 formation regimes threshold range is [0.35, 0.65], whereas the threshold also varies with the region and season (Li et al., 2011; Wei et al., 2018; Xing et al., 2019)." Line 274-280

34. **Comments:** *Lines 469–472: The basic description of RO_2/HO_2 + NO chemistry and its role in O_3 formation is repeated multiple times throughout the manuscript. Please substantially reduce this repetitive textbook-level explanation.*

Reply: Thank you for your suggestion. We have condensed the descriptions.

"The OH-initiated oxidation of VOCs is one of the key propagation steps in the RO_x cycle, generating RO_2 radicals and triggering subsequent radical chain propagation reactions." Line 611-612

35. **Comments:** *Lines 484–486: The statement should be quantitatively supported. Please provide the relative contributions of each VOC class to the total OH + VOC reaction rate.*

Reply: Thank you for your suggestion. Figure 9 has quantitatively presented the reaction rates of OH

radicals with the individual VOC classes, allowing their relative importance in the total OH + VOC reactivity to be assessed.

36. **Comments:** *Figure 10 and Lines 517–524: Please clarify what species are included in the "BVOC" category. If BVOC represents only isoprene, it would be clearer to label it as ISOP. If it includes other biogenic VOCs (e.g., terpenes), the discussion should not focus exclusively on isoprene and should address the contributions of the other BVOC species as well.*

Reply: Thank you for your suggestion. The species included in the BVOC category follow the classification used in the MEGAN framework, and the detailed species definitions can be found in the corresponding MEGAN documentation. Moreover, this BVOC category included terpenes. In the preceding discussion, we specifically examined the OH + isoprene reaction because isoprene is a representative biogenic VOC and was used here to help identify the key precursor species influencing O_3 formation at the urban and suburban sites. The detailed contributions of individual BVOC species are beyond the scope of the present study, as our main objective is to identify the key anthropogenic VOC categories and biogenic VOCs governing the urban–suburban differences in O_3 formation.

37. **Comments:** *Figure 10: It is unclear why the term "sensitivity coefficient" is used in the caption. Please define exactly what this coefficient represents and how it is calculated.*

Reply: Thank you for your suggestion. The term "coefficient" was somewhat redundant in this context. We have therefore removed the wording. CMAQ-DDM module and the interpretation of the calculated sensitivities have already been described in Section 2.2 WRF-CMAQ Modeling. For example, "Moreover, to identify key primary precursor emission driving O_3 formation, the Decoupled Direct Method in Three Dimensions (DDM-3D) module was used to calculate the sensitivities of O_3 to NO_x and primary VOC emission. CMAQ-DDM-3D can directly calculate the first-order sensitivity of pollutant concentrations to emission changes, eliminating the need for re-simulations and greatly reducing computational costs and simulation uncertainties (Cohan et al., 2005; Dunker, 1984; Dunker et al., 2002; Napelenok et al., 2006; Napelenok et al., 2008)." at line 201-207

38. **Comments:** *Line 507: "O_3 production" appears to be incorrect here. The DDM analysis in Figure 10 represents the sensitivity of O_3 concentration to precursor emissions, not the sensitivity of the O_3 production rate.*

Reply: Thank you for your suggestion. We have revised this expression.
"We quantify the first-order sensitivities of O_3 concentration to anthropogenic emissions" Line 658

39. **Comments:** *Lines 510–512: This statement appears abrupt and overinterprets the DDM results. Figure 10 shows emission sensitivities, not direct source contributions to O_3 formation. Please revise the wording and clarify how this conclusion follows from the sensitivity analysis.*

Reply: Thank you for your suggestion. We agree that the previous wording somewhat overinterpreted the DDM results. Figure 10 represents the sensitivity of O_3 to perturbations in different VOC emission

categories rather than their direct contributions to O_3 formation. We have therefore revised the corresponding text and instead describe the results in terms of O_3 sensitivity.

"Among the VOC categories, anthropogenic aromatics and alkenes were associated with the highest O_3 sensitivities at the urban site, whereas BVOC emissions showed the highest sensitivity at the suburban site. Alkane emissions exhibiting relatively weak sensitivities at both sites." Line 665-667

40. **Comments:** *Lines 512–516 and Figure 10: The interpretation of the reported first-order sensitivities is unclear. Although the sensitivities are given in ppbv, the manuscript does not define the emission perturbation or scaling parameter with respect to which they are calculated. Please provide the mathematical definition and explain what magnitude of emission change the reported sensitivity values correspond to.*

Reply: Thank you for your suggestion. Unlike the conventional brute-force approach, CMAQ-DDM-3D does not require an explicit finite emission perturbation (e.g., ±10% or ±20%) to be prescribed. Instead, DDM directly calculates the first-order derivative of pollutant concentration with respect to a defined emission scaling parameter under the base-case conditions. CMAQ-DDM-3D and the interpretation of the calculated sensitivities have already been described in Section 2.2 WRF-CMAQ Modeling. For example, "Moreover, to identify key primary precursor emission driving O_3 formation, the Decoupled Direct Method in Three Dimensions (DDM-3D) module was used to calculate the sensitivities of O_3 to NO_x and primary VOC emission. CMAQ-DDM- 3D can directly calculate the first-order sensitivity of pollutant concentrations to emission changes, eliminating the need for re-simulations and greatly reducing computational costs and simulation uncertainties (Cohan et al., 2005; Dunker, 1984; Dunker et al., 2002; Napelenok et al., 2006; Napelenok et al., 2008)" at line 200-206

41. **Comments:** *Line 517: "Higher OH reactivity of ISOP" is not appropriate here. Figure 9 shows the OH + ISOP reaction rate, not OH reactivity. Please revise the terminology accordingly.*

Reply: Thank you for your suggestion. The original sentence has already been deleted, so no further revision is needed here.

42. **Comments:** *Lines 517–524: The explanation for the greater BVOC sensitivity under urban high-NO_x conditions is plausible but remains qualitative. Please provide quantitative evidence linking BVOC-derived radical fate or RO_2 + NO chemistry to the enhanced O_3 sensitivity rather than inferring this solely from the general radical termination patterns.*

Reply: Thank you for your suggestion. We clarify that the greater O_3 sensitivity to BVOC emissions under urban high-NOx conditions is directly quantified by the first-order sensitivities shown in Figure 10, where the corresponding sensitivity values are explicitly reported. Thus, this conclusion is not inferred solely from the general radical termination patterns. In addition, the CMAQ-DDM-3D can quantify the sensitivity of O_3 concentrations to emission perturbations and cannot directly provide changes in individual chemical reaction rates associated with these sensitivities. Therefore, a direct quantitative attribution of the DDM-3D sensitivity to specific reaction-rate changes cannot be obtained

from the DDM-3D results alone.

Technical corrections:

1. **Comments:** *Throughout: Use consistent chemical formatting, including appropriate subscripts and superscripts.*

Reply: Thank you for your suggestion. We have systematically reviewed the entire manuscript and corrected all chemical formula.

2. **Comments:** *Line 38: Please change 'via radiative effect' to 'because of its radiative effects.'*

Reply: Thank you for your suggestion. We have revised the sentence accordingly.

"Tropospheric O_3 is also a significant greenhouse gas because of radiative effects" Line 41-42

3. **Comments:** *Lines 39-40: Please remove the marked unnecessary article, change 'scientific communities' to 'scientific community,' change 'has remained a focus of sustained attention' to 'has received sustained attention,' and replace 'governments' with 'policymakers.'*

Reply: Thank you for your suggestion. We have revised the sentence accordingly.

"O_3 has received sustained attention from the scientific community and policymakers over the past decades." Line 43-44

4. **Comments:** *Lines 41-43: Please replace 'As' with 'Because of' or 'Due to' and revise the verb agreement in the sentence, including 'ozone concentrations have remained.'*

Reply: Thank you for your suggestion. As the original sentence has already been removed during the revision process, no further modification is made here.

5. **Comments:** *Line 47: Please change 'once O3 formed' to 'once O3 is formed.'*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original phrasing has been omitted from the revised text. Consequently, no direct revision was applied to that sentence.

6. **Comments:** *Line 48: Please remove the extra parenthesis and 'e.g.' before R1-R3.*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original phrasing has been omitted from the revised text. Consequently, no direct revision was applied to that sentence.

7. **Comments:** *Lines 49-50: Please remove the redundant use of 'radical(s)' in the definitions of HO2 and RO2.*

Reply: Thank you for your suggestion. We have removed the redundant use of 'radical(s)' in the definitions of HO_2 and RO_2.

"where RO_x denotes the sum of hydroxyl radicals (OH), hydroperoxyl radicals (HO_2), and organic peroxy radicals (RO_2)" Line 51-52

8. **Comments:** *Lines 52-53: Please replace 'Under the action of' with 'Through' and revise 'formed' to 'represented,' as marked in the annotated manuscript.*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original phrasing has been omitted from the revised text. Consequently, no direct revision was applied to that sentence.

9. **Comments:** *Line 59: Please revise 'the ROx radicals cycle' to 'the ROx cycle.'*

Reply: Thank you for your suggestion. As the original sentence has already been removed during the revision process, no further modification is made here. To ensure terminological consistency throughout the manuscript, we have systematically reviewed the full text and revised all instances of the phrase "*ROx radicals cycle*" to "*ROx cycle*".

10. **Comments:** *Line 63: Please replace the second 'and' with 'as well as' in the list of primary ROx sources.*

Reply: Thank you for your suggestion. In order to response to the reviewers' comments, we have moved the detailed description of the atmospheric photochemistry to the Section 2.4 and Section 2.5. Section 2.5 has been added for describing the diagnostic analysis of the RO_x budget to facilitate the reader's understanding of the RO_x budget. We have revised the sentences accordingly.

"The main sources of primary RO_x radicals that initiate the RO_x cycle include the $O(^1D)$ channel of O_3 photolysis, and photolysis of HONO, HCHO, and other carbonyls, as well as the ozonolysis of alkenes" Line 255-257

11. **Comments:** *Line 65: Please remove the redundant word 'radicals' after OH.*

Reply: Thank you for your suggestion. To ensure terminological consistency throughout the manuscript, we have systematically reviewed the full text and revised all instances of the redundant phrase "OH radicals" or "HO_2 radicals".

12. **Comments:** *Line 66: O3 photolysis does not directly produce OH; it first generates $O(^1D)$, which subsequently reacts with water vapor to form OH. Therefore, please change 'by O3 photolysis at wavelengths below 320 nm (R6-R7) in the troposphere' to 'through O3 photolysis at wavelengths below 320 nm (R6-R7), followed by the reaction of $O(^1D)$ with water vapor in the troposphere.'*

Reply: Thank you for your suggestion. In order to response to the reviewers' comments, we have moved the detailed description of the atmospheric photochemistry to the Section 2.4 and Section 2.5. In the corresponding sections, we have corrected the descriptions.

"Conversely, O_3 loss pathways include O_3 photolysis to $O(^1D)$ (followed by the reaction of $O(^1D)$ with water vapor) and ozonolysis of alkenes, and reactions with OH and HO_2. Additionally, the reaction of NO_2 with OH, which effectively removes NO_x from the cycle by forming HNO_3, is also accounted for

one of the O_3 loss pathways. The total O_3 destruction rate ($D(O_3)$) is determined by Equation (2).

$$D(O_3) = j_{O^1D}[O_3] \times fac + k_{[O_3,Alkenes]}[Alkenes][NO] + k_{[O_3,OH]}[O_3][OH] + k_{[O_3,HO_2]}[O_3][HO_2] + k_{[NO_2,OH]}[NO_2][OH] \quad (2)$$

$$fac = \frac{k_{[O(^1D),H_2O]}[H_2O]}{\left(k_{[O(^1D),O_2]}[O_2] + k_{[O(^1D),N_2]}[N_2] + k_{[O(^1D),H_2O]}[H_2O]\right)}$$

It noted that the first term for O_3 photolysis in Equation (2) is only including the reaction of $O(^1D)$ with H_2O to generate OH, which leads to net O_3 loss. Other $O(^1D)$ loss channels (e.g., quenching by N_2 or O_2) regenerate O_3 through $O(^3P) + O_2$ and thus have no net effect on O_3 destruction, resulting in that they are excluded from this term accordingly." Line 244-253

"The main sources of primary RO_x radicals that initiate the RO_x cycle include the $O(^1D)$ channel of O_3 photolysis, and photolysis of HONO, HCHO, and other carbonyls, as well as the ozonolysis reaction of O_3 with alkenes" Line 255-257

13. **Comments:** *Line 69: Please change 'VOC' to 'VOCs.'*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original sentence has been removed. Furthermore, to ensure terminological consistency throughout the paper, we have carefully re-examined the entire text and corrected all instances where "VOC" should be used as a plural noun to "VOCs.

14. **Comments:** *Line 70: The reference to Reaction R9 should be changed to R10.*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original sentence has been removed.

15. **Comments:** *Line 80: Please remove the redundant phrase 'mutual self-reaction.'*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original sentence has been removed.

16. **Comments:** *Line 81: Please replace 'explosive' with an appropriate noun phrase, such as 'explosive growth.'*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the relevant paragraph in response to the reviewers' comments. The original sentence has been removed.

17. **Comments:** *Line 86: Please change 'ratio' to 'ratios' and revise the corresponding pronoun to 'their.'*

Reply: Thank you for your suggestion. In the revised manuscript, we have substantially condensed the

relevant paragraph in response to the reviewers' comments. The original sentence has been removed.

18. **Comments:** *Reaction R13: Please change NO2 to NO, consistent with the chemical correction described in Specific comment 5.*

Reply: Thank you for your suggestion. We have corrected the Reaction 13 in the manuscript, corresponding to Reaction 16 in Table S1 of the revised manuscript.

$$RO_2 + NO \rightarrow RONO_2 \quad \text{(R16)}$$

19. **Comments:** *Line 97: Please change 'laboratory simulations' to 'laboratory experiments.'*

Reply: Thank you for your suggestion. We have corrected the expression.

"Given the limitations of field observations or laboratory experiments in fully representing O_3 regional characteristics" Line 56-57

20. **Comments:** *Lines 99-100: Please change 'the air quality model' to 'air quality models' and 'largely' to 'strongly.'*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process; therefore, no further revision is made here.

21. **Comments:** *Line 104: Please revise 'As far' to 'So far' or remove the expression.*

Reply: Thank you for your suggestion. We have removed the expression at line 66.

22. **Comments:** *Line 107: Please remove 'and so on.'*

Reply: Thank you for your suggestion. We have removed 'and so on' at line 69.

23. **Comments:** *Lines 108-110: Please revise the classification sentence to state that photochemical mechanisms are 'classified as explicit or lumped.' Change 'Explicit reaction mechanism' to 'An explicit reaction mechanism.'*

Reply: Thank you for your suggestion. We have corrected these expressions.

"From the perspective of chemical species, these photochemical mechanisms are generally classified as explicit or lumped mechanisms" Line 70-71

"An explicit reaction mechanism includes all species involved in a chemical reaction" Line 71-72

24. **Comments:** *Line 112: Please remove the extraneous words in 'the mainstream choices for in the air quality model.'*

Reply: Thank you for your suggestion. We have corrected these expressions.

"lumped chemical mechanisms such as CBM, SAPRC and RACM are the mainstream choices in the air quality model." Line 74-75

25. **Comments:** *Lines 115-116: Please change 'research' to 'studies.'*

Reply: Thank you for your suggestion. We have corrected the expression.

"The CBM classified by carbon-bond structures is the most widely applied chemical mechanism in air quality modeling studies for its low computational cost and the relative ease of obtaining emission inventories" Lin 78-80

26. **Comments:** *Lines 119-120: Please remove the redundant word 'requirement,' change 'limit' to 'limits,' and consider citing the recent mechanism-evaluation study https://doi.org/10.5194/gmd-18-8461-2025.*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process; therefore, no further revision is made here. We have added citations to the relevant articles mentioned above.

"Unlike the highly lumped CBM, the SAPRC mechanism classifies organic species according to their OH reactivity, features the detailed description of reactions involving specific VOC and provides a more mechanistically explicit treatment of peroxy radical (Carter, 2010b; Carter et al., 2025)." Line 87-90

"Carter, W. P. L., Jiang, J., Wang, Z., and Barsanti, K. C.: The SAPRC atmospheric chemical mechanism generation system (MechGen), Geosci. Model Dev., 18, 8461-8483, 10.5194/gmd-18-8461-2025, 2025."

27. **Comments:** *Line 123: Please change 'which often referred' to 'which are often referred.'*

Reply: Thank you for your suggestion. We have corrected the expression.

"minimizes reliance on lumped species which are often referred as operators for radical cycle" Line 102

28. **Comments:** *Line 126: Please remove the sentence fragment beginning 'And RACM...' or integrate it grammatically into the preceding sentence.*

Reply: Thank you for your suggestion. We have integrated it into the preceding sentence to improve grammatical coherence.

"These attributes make RACM2 particularly well-suited for comparison with observational data, ensure transparency in the mapping of emission inventories, and provide flexibility for modification and further expansion, while maintaining computational efficiency comparable to that of SAPRC mechanisms and suitable for regulatory applications." Line 103-106

29. **Comments:** *Lines 131-132: Please change 'Previous study has evaluated' to 'Previous studies have evaluated.'*

Reply: Thank you for your suggestion. In order to response to the reviewers' comments, we have substantially rewritten this section of the manuscript. The original sentence has been removed.

30. **Comments:** *Lines 137-139: Please change 'other study' to 'other studies,' replace 'for more detailed VOC treatment' with 'due to/owing to the more detailed VOC treatment,' and change 'a recent comparative study using box models have demonstrated' to 'a recent comparative study using box*

models has demonstrated.'

Reply: Thank you for your suggestion. We have corrected these expressions.

"due to the more detailed VOC treatment in SAPRC07. Moreover, a recent comparative study using box models has demonstrated that CB06 and SAPRC07 both tended to underestimate OH than RACM2" Line 115-117

31. **Comments:** *Lines 141-143: Please revise to: 'However, few studies have investigated uncertainties in simulations of O3 pollution over China using three-dimensional air-quality models that arise from different photochemical mechanisms.'*

Reply: Thank you for your suggestion. In order to response to the reviewers' comments, we have substantially rewritten this section of the manuscript. The original sentence has been removed.

32. **Comments:** *Line 144: Please write the area as '14,335 km².'*

Reply: Thank you for your suggestion. We have corrected this expression.

"a megacity in southwest China, covers a total area of about 14,335 km^2" Line 126

33. **Comments:** *Lines 145-146: Please correct 'GPD' to 'GDP' and identify the currency used for '2.35 trillion dollars' (e.g., CNY).*

Reply: Thank you for your suggestion. We have corrected these expressions.

"In recent years, the total gross domestic product (GDP) of Chengdu was increasing rapidly, around 2.35 trillion dollars CNY in 2024" Line 127-128

34. **Comments:** *Lines 147-149: Please revise the description to 'as a major regional center in western China,' change 'expected' to 'is expected to become,' and change 'Its features' to 'It features.'*

Reply: Thank you for your suggestion. We have corrected these expressions.

"It is designated as a major regional center in western China, and expected to become one of the economic centers in western China. It features dense urban population," Line 129-130

35. **Comments:** *Figure 1b: Please use a subscript in NO2.*

Reply: Thank you for your suggestion. We have revised the expression.

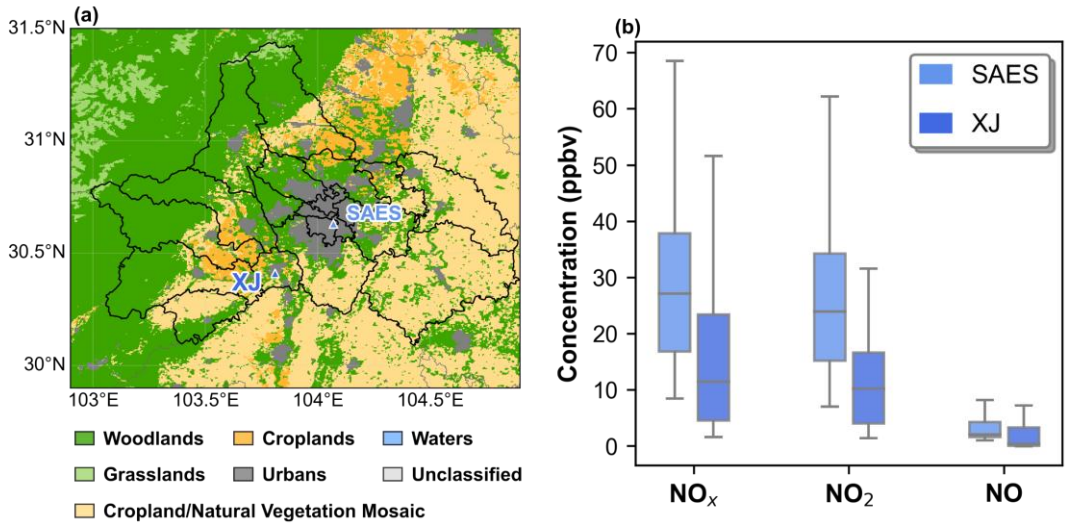


Figure 6 (a) Land use types in Chengdu and surrounding areas, along with the locations of the SAES site (light blue triangle) and XJ site (dark blue triangle). (b) Distribution of NO_x (NO_x = NO +NO_2), NO_2 and NO concentrations (ppbv) at the Sichuan Academy of Environmental Sciences (SAES) site and Xinjin (XJ) site during this pollution episode. The box plots present the 10th, 25th, 50th, 75th, and 90th percentiles of the statistical metrics individually.

36. **Comments:** *Line 216: Please check whether 'RADM2' should be 'RACM2.'*

Reply: Thank you for your suggestion. We confirm that the VOC speciation profiles utilized in this study, which are derived from the MEIC inventory, are indeed based on the RADM2 (Regional Acid Deposition Model version 2) mechanism, rather than RACM2. To avoid any potential confusion arising from the nomenclature and evolutionary relationship between RADM2 and RACM2 (noting that RACM2 is a later development from the RADM2 lineage), we have added a clear clarification in the Introduction section.

37. **Comments:** *Figure 2: Please mark XJ and use a consistent simulation period (August 9-18 versus August 9-19).*

Reply: Thank you for your suggestion. Regarding the simulation period, we have checked the descriptions and confirm that all simulations consistently cover the period (August 9-18). Regarding the marking of the XJ site, we have already clearly labeled its geographic location in Figure 1. Repeating the geographic coordinate marker in Figure 2 would be visually redundant. Therefore, we opted not to mark it in Figure 2.

38. **Comments:** *Line 276: Please change 'In specific' to 'Specifically.'*

Reply: Thank you for your suggestion. We have corrected the expression, as shown in line 290.

39. **Comments:** *Line 281: Please change 'Previous study' to 'A previous study.'*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process; therefore, no further revision is made here.

40. **Comments:** *Line 377: Please change 'literature' to 'a literature value' or another grammatically appropriate expression.*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process; therefore, no further revision is made here.

41. **Comments:** *Line 429: Please change 'In specific' to 'Specifically' and replace 'in Zhou's research (Zhou et al., 2024)' with 'consistent with Zhou et al. (2024).'*

Reply: Thank you for your suggestion. We have corrected the expression.

"At the urban site, HONO photolysis was the dominant primary RO_x source, accounting for 29.2%–35.2% of P(RO_x), consistent with the important role of HONO photolysis under polluted urban conditions reported by Zhou et al. (2024)" Line 533-535

42. **Comments:** *Lines 430-431: Please revise the sentence connection by replacing the period before 'And' with a comma and continuing with 'and.'*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process; therefore, no further revision is made here.

43. **Comments:** *Line 433: Please check the marked article and capitalization in 'O3 and Alkenes' and remove the extra 'and' after the HCHO-photolysis contribution.*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process. However, we have carefully checked the entire manuscript for similar issues and revised the relevant text where necessary.

44. **Comments:** *Lines 434-436: Please provide numerical support for 'significantly higher,' replace 'hydroxyl compounds' with 'carbonyl compounds' if that is the intended meaning, and remove the unnecessary phrase 'rate parameters of.'*

Reply: Thank you for your suggestion. The original sentence has already been removed during the revision process. However, we have added numerical support for "significantly higher" as requested.

"Among these pathways, the most pronounced inter-mechanistic difference occurred in the photolysis of other carbonyl compounds. Its contribution reached 26.3% in RACM2, compared with 20.7%–22.5% in SAPRC07 and CB06, corresponding to production rates of 2.1, 1.6, and 1.4 ppbv h^{-1} for RACM2, SAPRC07, and CB06, respectively." Line 539-542

45. **Comments:** *Line 451: Please replace 'OH-HO2-RO2 radical system' with 'ROx radical system.*

Reply: Thank you for your suggestion. We have corrected this expression.

"Previous work also reported that RO_x radical termination in Chengdu was dominated by reactions of OH with NO_x" Line 567-568

46. **Comments:** *Section 3.3.1: Please reorganize the text into logically distinct paragraphs separating*

general findings, quantitative comparisons, and mechanistic interpretation.

Reply: Thank you for your suggestion. We have reorganized Section 3.3.1 to improve the logical flow and readability. The revised section is now structured into distinct paragraphs that separately present (1) the general findings and overall inter-mechanistic patterns, (2) the quantitative comparisons of O_3 formation and loss rates and the identification of their major pathways for the differences among the mechanisms, and (3) the mechanistic interpretation of these differences, including their relationships with simulated radical concentrations and mechanism-dependent RO_x chemistry. This restructuring provides a clearer progression from the overall results to the quantitative evidence. Detailed revisions are provided in the revised manuscript.

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