

Referee comments:

This manuscript presents an interesting study, investigating what is driving ozone production in the region of Zhengzhou. The authors have investigated both the reactivity of individual/grouped VOCs as well as a source apportionment analysis, and a box model has been used to produce an ozone production isopleth. Whilst these are the key sections crucial to any exploration of the O₃-NO_x-VOC relationships in an urban centre, the authors could work on adding some more detail to each section. In addition, more work is needed to bring together all of the results sections, with more discussion on what the data is telling us and what this could mean for what is driving ozone production. With these changes in place, I would recommend this manuscript for publication in the Journal of Atmospheric Chemistry and Physics.

This manuscript is generally well written, with a small number of couple of grammatical mistakes (e.g. line 74: is in a VOCs-limited regimes, change to “is in a VOC-limited regime”).

Some conclusions are made throughout the manuscript that are not so clearly backed up by the results. The authors could add some more quantification (e.g. percentage differences), when comparing Case 1, Case 2 and clean days. If the main message is that the sources are the same during both polluted and clean days, this needs to be made clearer. If this

is the case, what could be driving the ozone production? Is it elevated concentrations? Could it be temperature? This can all be brought together in the conclusions.

The authors should include an expanded version of Table 1, which shows average mixing ratios for all the VOCs measured. It should also be made clear which of these VOCs are used in which part of the study (e.g. OBM, source apportionment etc.). The should be made available in the supplementary.

The authors should also consider changing the title from “central plain city, China” to the name of the city (Zhengzhou) for clarity.

To improve the coherency of the manuscript, the authors should bring together findings from previous sections into the next section. For example, there are sections on concentrations and sources of a variety of VOCs, but then the last results section ignores that knowledge and just focuses on varying AVOCs by bulk.

The author should incorporate the results from previous sections into this last section. For example, how does O₃ production change when NO_x is varied alongside reductions in each source respectively? The conclusions should bring together all of the findings of each results section.

Reviewers' comments:

Thank you for your careful reading of our paper and valuable comments

and suggestions. We believe that we have adequately addressed your comments. To facilitate your review, the comments are in black, and the responses are in blue. The major changes that have been made according to these responses were marked in yellow color in the highlighted copy of the revised manuscript. And our own minor changes were marked in red font. Note that the following line numbers are shown in the corrected version.

Response: Thank you for your careful reading of our paper and valuable comments and suggestions. We believe that we have adequately addressed your comments. To facilitate your review, the comments are in black, and the responses are in blue. The major changes that have been made according to these responses were marked in yellow color in the highlighted copy of the revised manuscript. And our own minor changes were marked in red font. Note that the following line numbers are shown in the corrected version.

We have made the corrections as per your suggestions by fixing the grammatical errors and changing the title from "central plain city, China" to the city name (Zhengzhou) for clarity. Thank you for your valuable feedback, these modifications will enhance the clarity and accuracy of the manuscript. Furthermore, in response to the comments of reviewer 1, we have revised the abbreviation in

the manuscript from "VOCs" to "NMVOCs" as recommended. But, in Section 3.3, we further differentiate NMVOCs into AVOC and BVOC. The abbreviations for AVOCs and BVOCs remain unchanged.

Major comments:

44 Remove "of course"

Response: Thanks for the suggestion. It has been deleted.

199 Although I recognise that additional details on the GC-MS instrumentation can be found in a previous publication, the authors should include a few more details about instrumentation in the sample collection section. What is the time resolution of samples? How long were samples captured for? What were they captured in, and how long were they left before being analysed by the instrumentation?

Response: Thanks for the comments.

I have included more details about the GC-MS instrumentation in the sample collection section, addressing the time resolution of samples. (Section 2.2. Line 120-128).

Line 120-128: The time resolution of the instrument is 1 hour, and the flow rate is 60 mL/min. The air sample was collected for the

first 5 minutes of each hour and then pre-concentrated through a cold trap to remove H₂O₂ and CO₂. The sample was captured using an empty capillary column. After pre-concentration, the sample was desorbed by rapid heating and introduced into an analytical system. After separation by chromatographic column, the sample was detected by FID (for C₂-C₅ hydrocarbons) and MS (for C₅-C₁₂ hydrocarbons, halocarbons and OVOCs). The correlation coefficient of the standard curve of the target compound was greater than or equal to 0.99, and the detection limit of the instrument method was less than or equal to 0.1 nmol/mol. A total of 115 NMVOCs were monitored, including 29 alkanes, 11 alkenes, 1 alkyne, 17 aromatic hydrocarbons, 35 halogenated hydrocarbons, 21 OVOCs and 1 sulfide (carbon disulfide).

147 CPF is described as a “new source identification tool”, but papers from 2006 and 2007 are referenced. Is this technique new? Have there been new applications of this?

Response: Sorry for the confusing and thanks for suggestions.

CPF is not a new technology. CPF analysis was applied to show the relative location of potential emission sources by using the wind directions and source contributions calculated by PMF (Kim and Hopke, 2004). We have revised the CPF description and changed

the references in the relevant literature. (Line 155-158)

Line 155-158: The conditional probability function (CPF) is a source identification tool, which can be used to identify local emission sources of pollutants (Uria-Tellaetxe and Carslaw, 2014). CPF analysis methods were employed to determine the potential direction of emission sources by utilizing the wind directions and source contributions calculated through PMF (Kim and Hopke, 2004).

154 The MCM is no longer hosted at the University of Leeds and hasn't been for a while. I suggest you provide the new working link, hosted by the University of York (<https://mcm.york.ac.uk/MCM/>). (Line 160)

Response: Sorry for the mistake.

we have updated the link to the new working website hosted by the University of York (<https://mcm.york.ac.uk/MCM/>).

164 The authors should also describe how they have calculated $P(O_3)$ from the model, if this was not a direct output. If the authors are using a specific box model (e.g. DSMACC, AtChem2), please specify which one and include the appropriate references.

Response: Thanks for the suggestion.

In this study, the net production rate O_3 ($P(O_3)$) is the difference between the O_3 production (the oxidation of NO by HO_2 and RO_2) and O_3 destruction (O_3 photolysis, reactions of O_3 with OH and HO_2 , reactions of OH with NO_2 , and reactions of O_3 with alkenes). This method for estimating O_3 production and removal rates has been utilized in several previous studies (Wang et al., 2017; Wang et al., 2022). The constants (k) represent the rate coefficients of the respective reactions, as follows:

$$P(O_3) = [k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_{2i}+NO}[RO_{2i}][NO] - k_{HO_2+O_3}[HO_2][O_3] - k_{OH+O_3}[OH][O_3] - k_{O(^1D)+H_2O}[O(^1D)][H_2O] - k_{OH+NO_2}[OH][NO_2] - k_{alkenes+O_3}[alkenes][O_3]$$

The details of this calculation method have been included in the revised manuscript along with the appropriate references. Thank you for highlighting this important aspect of our methodology. (Line 170-176)

We did not use a specific box model such as DSMACC or AtChem2 in our study. Our model is a 0-D box model incorporating the Master Chemical Mechanism version 3.3.1 (MCMv3.3.1). This model can simulate the concentration of radicals in the atmosphere and has been widely used to calculate the production of O_3 , as well as budgets of radicals and intermediate species. Additionally, the

studies by Wang et al. (2022) and Guo et al. (2024) provide detailed descriptions of this model.

Line 172-178: In this model, the net production rate O_3 ($P(O_3)$) is the difference between the O_3 production (the oxidation of NO by HO_2 and RO_2) and O_3 destruction (O_3 photolysis, reactions of O_3 with OH and HO_2 , reactions of OH with NO_2 , and reactions of O_3 with alkenes). This method for estimating O_3 production and removal rates has been utilized in several previous studies (Wang et al., 2022; Guo et al., 2024). The constants (k) represent the rate coefficients of the respective reactions, as follows:

$$\begin{aligned}
 P(O_3) = & [k_{HO_2+NO} [HO_2] [NO] + \sum k_{RO_2i+NO} [RO_{2i}] [NO] - \\
 & k_{HO_2+O_3} [HO_2] [O_3] - k_{OH+O_3} [OH] [O_3] - k_{O(^1D)+H_2O} [O(^1D)] [H_2O] - \\
 & k_{OH+NO_2} [OH] [NO_2] - k_{alkenes+O_3} [alkenes] [O_3] \quad (8)
 \end{aligned}$$

170 Was any interpolation or averaging of the data performed to generate 1 h time resolution data for the model?

Response: Thanks for the suggestion.

All the species we monitored were at a 1 h time resolution. We did not interpolate or average the data, and the observation-based data we entered into the model were all at 1 h time resolution. At the same time, in the mode, we set the step length of the mode to be 1 hour, so the result of the mode output is also 1 hour time resolution.

171 Why was WS constrained in your box model? This parameter is not used by the

MCM. Was it used to calculate other factors in your model?

Response: Thanks for the comments.

WS was really constrained in our box model. In our model, we take into account the effect of horizontal transmission on pollution transmission, which makes our simulation results more accurate.

172 Please list all the measured VOCs, indicating which ones were selected, in a table. It would also be helpful to see average concentrations for these compounds. All of this should be presented in the supplementary.

Response: Thanks for the suggestion.

We have included a table (Table S1) in the supplementary material listing all the measured NMVOCs and indicating the selected compounds along with their average concentrations. We hope this additional information meets your requirements.

Table S1. Results of NMVOCs observed: concentrations with statistical analysis, ppbv.

Groups	Species	Mean \pm SD	Median	25%	75%	MCM v3.3.1 name
Alkanes						
	Ethane	3.52 \pm 1.58	3.07	2.28	4.41	C2H6
	Propane	1.68 \pm 0.9	1.44	1.03	2.12	C3H8
	Isobutane	0.9 \pm 0.59	0.73	0.5	1.13	IC4H10
	n-butane	1.1 \pm 0.75	0.9	0.59	1.34	NC4H10
	Isopentane	1.01 \pm 0.64	0.84	0.6	1.23	IC5H12

	n-Pentane	0.48 ± 0.39	0.38	0.26	0.55	NC5H12
	2,2-Dimethylbutane	0.02 ± 0.02	0.02	0.01	0.03	M22C4
	Cyclopentane	0.08 ± 0.04	0.07	0.05	0.09	
	2,3-Dimethylbutane	0.03 ± 0.02	0.03		0.04	M23C4
	2-Methylpentane	0.17 ± 0.11	0.14	0.1	0.2	M2PE
	3-Methylpentane	0.1 ± 0.09	0.08	0.06	0.12	M3PE
	n-Hexane	0.62 ± 0.36	0.56	0.38	0.77	NC6H14
	Methylcyclopentane	0.04 ± 0.03	0.03	0.02	0.04	
	2,4-Dimethylpentane	0.01 ± 0.01	0.01	0.01	0.01	
	Cyclohexane	0.03 ± 0.02	0.02	0.01	0.03	CHEX
	2-Methylhexane	0.01 ± 0.01	0.01	0.01	0.02	M2HEX
	2,3-Dimethylpentane	0.01 ± 0.01	0.01	0.01	0.01	
	3-Methylhexane	0.01 ± 0.01	0.01	0.01	0.02	M3HEX
	2,2,4-Trimethylpentane	0.02 ± 0.02	0.02	0.01	0.02	
	n-Heptane	0.01 ± 0.01	0.01	0.01	0.02	NC7H16
	Methylcyclohexane	0.02 ± 0.02	0.02	0.01	0.03	
	2,3,4-Trimethylpentane	0.01 ± 0.01	0.01	0.01	0.01	
	2-Methylheptane	0.01 ± 0	0	0	0.01	
	3-Methylheptane	0.01 ± 0	0.01	0	0.01	
	Octane	0.02 ± 0.02	0.01	0.01	0.02	NC8H18
	n-Nonane	0.01 ± 0.01	0.01	0.01	0.01	NC9H20
	n-Decane	0.01 ± 0	0.01	0.01	0.01	NC10H22
	Undecane	0.01 ± 0	0.01	0.01	0.01	NC11H24
	Dodecane	0.01 ± 0	0.01	0.01	0.01	NC12H26
Alkenes						
	1-Hexene	0.13 ± 0.3	0.04	0.03	0.06	HEX1ENE
	Ethylene	0.89 ± 0.52	0.82	0.49	1.14	C2H4
	Propylene	0.45 ± 0.57	0.22	0.12	0.66	C3H6
	trans-2-Butene	0.03 ± 0.02	0.02	0.02	0.03	TBUT2ENE
	1-Butene	0.05 ± 0.03	0.04	0.04	0.06	BUT1ENE
	cis-2-Butene	0.02 ± 0.01	0.02	0.01	0.03	CBUT2ENE
	trans-2-Pentene	0 ± 0.01	0	0	0	TPENT2ENE
	1-Pentene	0.01 ± 0.01	0.01	0	0.01	PENT1ENE
	cis-2-Pentene	0.01 ± 0.01	0	0	0.01	CPENT2ENE
	Isoprene	0.38 ± 0.54	0.14	0.02	0.52	C5H8
	1,3-Butadiene	0.01 ± 0.01	0.01	0.01	0.02	C4H6
Alkynes						
	Ethyne	1.07 ± 0.58	0.95	0.63	1.42	C2H2
Aromatics						
	Benzene	0.29 ± 0.14	0.25	0.19	0.36	BENZENE
	Toluene	0.47 ± 0.33	0.36	0.25	0.57	TOLUENE
	Ethylbenzene	0.07 ± 0.05	0.05	0.03	0.08	EBENZ
	m/p-Xylene	0.14 ± 0.11	0.11	0.07	0.18	MXYL
	Styrene	0.01 ± 0.01	0.01	0	0.01	STYRENE

	o-Xylene	0.07 ± 0.06	0.05	0.03	0.09	OXYL
	Isopropyl benzene	0 ± 0	0	0	0	IPBENZ
	n-Propyl benzene	0.01 ± 0	0.01	0	0.01	PBENZ
	3-Ethyltoluene	0.01 ± 0.01	0.01	0.01	0.02	METHTOL
	4-Ethyltoluene	0.01 ± 0.01	0.01	0	0.01	PETHTOL
	1,3,5-Trimethylbenzene	0.01 ± 0	0.01	0	0.01	TM135B
	2-Ethyltoluene	0.01 ± 0	0.01	0	0.01	OETHTOL
	1,2,4-Trimethylbenzene	0.02 ± 0.02	0.02	0.01	0.03	TM124B
	1,2,3-Trimethylbenzene	0.01 ± 0.01	0.01	0	0.01	TM123B
	1,3-Diethylbenzene	0 ± 0	0	0	0	
	1,4-Diethylbenzene	0 ± 0	0	0	0.01	
	Naphthalene	0.01 ± 0.01	0.01	0.01	0.02	
Halohydrocarbons						
	Freon12	0.13 ± 0.02	0.13	0.12	0.13	
	Freon114	0.12 ± 0.02	0.12	0.1	0.14	
	Chloromethane	0.64 ± 0.17	0.61	0.52	0.73	CH3CL
	Vinyl chloride	0.02 ± 0.04	0.01	0.01	0.02	VINCL
	Bromomethane	0.01 ± 0	0.01	0.01	0.01	CH3BR
	Chloroethane	0.02 ± 0.01	0.02	0.02	0.03	CH3CH2CL
	Freon11	0.21 ± 0.02	0.21	0.21	0.22	
	1,1-Dichloroethylene	0 ± 0	0	0	0	CCL2CH2
	Freon113	0.07 ± 0.01	0.07	0.07	0.08	
	Dichloromethane	1.06 ± 1.2	0.89	0.67	1.23	CH2CL2
	1,1-Dichloroethane	0.08 ± 0.08	0.06	0.04	0.09	CHCL2CH3
	cis-1,2-Dichloroethylene	0 ± 0	0	0	0	CDICLETH
	Chloroform	0.74 ± 0.55	0.58	0.35	0.95	CHCL3
	1,1,1-Trichloroethane	0 ± 0	0	0	0	CH3CCL3
	Tetrachloromethane	0.09 ± 0.01	0.09	0.09	0.1	
	1,2-Dichloroethane	0.51 ± 0.33	0.42	0.31	0.62	CH2CLCH2CL
	Trichloroethylene	0.01 ± 0	0.01	0	0.01	TRICLETH
	1,2-Dichloropropane	0.19 ± 0.16	0.15	0.11	0.22	CL12PROP
	Bromodichloromethane	0 ± 0	0	0	0	
	trans-1,3-Dichloropropene	0.01 ± 0.01	0.01	0	0.01	
	cis-1,3-Dichloropropene	0 ± 0	0	0	0	
	1,1,2-Trichloroethane	0.03 ± 0.03	0.03	0.02	0.04	CH2CLCHCL2
	Tetrachloroethylene	0.32 ± 0.36	0.21	0.1	0.41	TCE
	1,2-Dibromoethane	0 ± 0	0	0	0	DIBRET
	Chlorobenzene	0.01 ± 0	0.01	0.01	0.01	

	Bromoform	0 ± 0	0	0	0	
	1,1,2,2-Tetrachloroethane	0 ± 0	0	0	0	CHCL2CHCL2
	1,3-Dichlorobenzene	0 ± 0	0	0	0	
	1,2-Dichlorobenzene	0 ± 0	0	0	0	
	trans-1,2-Dichloroethylene	0.01 ± 0	0	0	0.01	
	Dibromochloromethane	0 ± 0	0	0	0	
	1,4-Dichlorobenzene	0.02 ± 0.01	0.02	0.01	0.02	
	Benzyl chloride	0 ± 0	0	0	0	
	1,2,4-Trichlorobenzene	0 ± 0	0	0	0	
	Hexachloro-1,3-butadiene	0.01 ± 0	0.01	0.01	0.01	
OVOCs	acetaldehyde	0.2 ± 0.15	0.16	0.1	0.24	CH3CHO
	n-butyraldehyde	0.07 ± 0.1	0.05	0.04	0.06	
	1,4-Dioxane	0.01 ± 0	0.01	0	0.01	
	Acrolein	0.14 ± 0.07	0.12	0.09	0.16	ACR
	propanal	0.33 ± 0.1	0.33	0.26	0.4	C2H5CHO
	Acetone	2.74 ± 0.7	2.78	2.25	3.2	CH3COCH3
	MTBE	0.04 ± 0.04	0.03	0.02	0.04	MTBE
	methylacrolein	0.1 ± 0.09	0.08	0.06	0.12	MACR
	valeraldehyde	0.05 ± 0.02	0.05	0.04	0.06	C4H9CHO
	caproaldehyde	0.08 ± 0.06	0.07	0.02	0.11	
	Isopropanol	0.02 ± 0.02	0.02	0.01	0.03	IPROPOL
	Vinyl acetate	0 ± 0	0	0	0.01	
	Ethyl acetate	0.24 ± 0.2	0.19	0.13	0.3	ETHACET
	2-Butanone	0.24 ± 0.1	0.21	0.17	0.29	MEK
	Tetrahydrofuran	0.03 ± 0.02	0.02	0.01	0.03	
	Methyl methacrylate	0.01 ± 0	0.01	0	0.01	
	4-Methyl-2-pentanone	0.01 ± 0.01	0.01	0.01	0.02	MIBK
	2-Hexanone	0.22 ± 0.22	0.19	0.03	0.32	HEX2ONE
	Crotonaldehyde	0.02 ± 0.02	0.02	0.01	0.03	
	benzaldehyde	0.01 ± 0	0.01	0.01	0.01	
	m-methylbenzaldehyde	0 ± 0	0	0	0	
Sulfide	Carbon disulfide	0.13 ± 0.22	0.06	0.03	0.12	

173 What are the default values for $j(\text{H}_2\text{O}_2)$ and $j(\text{O}_1\text{D})$ and planetary boundary layer? Do you think these are representative of the site? Have any dilution rates been applied to compounds generated in the

model, and if so, are these varied based on the default PBLH? The authors need to highlight why these values were used. If measured or modelled values cannot be used, it is important to discuss the uncertainties associated with using default values for your results.

Response: Thanks for the suggestion.

We acknowledge the error in our manuscript where we incorrectly referred to $J(\text{NO}_2)$ instead of $J(\text{O}_1\text{D})$. We have since made the necessary corrections in the revised version of the manuscript.

In this study, the values of PBL, $J(\text{H}_2\text{O}_2)$, and $J(\text{NO}_2)$ we use are the results obtained from the model simulation. Although we did not have actual observational data, setting default values still helps improve the accuracy of our simulations. Compared to results without default values, the results with default values are more accurate and reliable. As mentioned in section 2.5 of the manuscript, we assessed the reliability of the simulation results by simulating the concentration of O_3 . We calculated the index of agreement (IOA) to be 0.8. Since the real atmospheric boundary layer is variable, changes in the boundary layer can lead to variations in pollutant concentrations. An increase in the boundary layer height results in dilution of pollutant concentrations, and the dilution ratio in the model is based on changes in the planetary boundary layer.

180 Please provide more context for why a value of 0.6 indicates the model is performing well. What is the acceptable range for this value to be? Which compound did you evaluate the performance of the model using? What was constrained in the model when you did this, and what was the model left to calculate. Much more detail is required here.

Response: Thanks for the suggestion.

The performance of the OBM was evaluated by applying the index of agreement (IOA). The calculation formula is as follows:

$$\text{IOA} = 1 - \frac{\sum_{i=1}^n (O_i - M_i)^2}{\sum_{i=1}^n (|O_i - \bar{O}| + |M_i - \bar{O}|)^2}$$

We evaluate the reliability of the model simulation results by simulating the concentration of O₃ in the atmosphere and calculating the IOA value. In the model, we do not input observations of O₃, but by input the concentrations of trace gases (SO₂, CO, and NO) and 75 NMVOCs, and meteorological parameters (T, RH, and WS) to simulate the concentration of O₃ in the atmospheric environment. Finally, the IOA value is calculated from the simulated and observed values.

We have consulted a lot of literature and made a comparative analysis with the IOA value in the literature. In many studies, when IOA

ranges from 0.68 to 0.89, the simulation results are reasonable (Wang et al., 2018;Liu et al., 2022). We calculated an IOA value of 0.6 using data from all days. In fact, O₃ is not produced at night, so we recalculated the IOA value from 7:00 to 19:00 during the day and obtained a result of 0.8. Therefore, the results simulated by our model are reliable. At the same time, we also modified 0.6 to 0.8 in the manuscript. (Line 197-203)

Line 197-203: In various studies, model simulation results are often considered acceptable when the value of IOA falls within the range of 0.68 to 0.89 (Wang et al., 2018). To evaluate the reliability of our model simulations, we conducted an analysis of O₃ concentration in the atmosphere and calculated the IOA value. Our model does not directly incorporate O₃ observations. Instead, it utilizes concentrations of trace gases (SO₂, CO, and NO) and 75 NMVOCs, and meteorological parameters (T, RH, and WS) to simulate the concentration of O₃ in the atmospheric environment. The IOA values for O₃ was calculated from 7:00 to 19:00 during the day and obtained a result of 0.8. Therefore, the results simulated by our model are reliable.

189 What is meant by “short pollution process”? Do you mean that the pollution event was too short, and you only looked at periods where pollution remained high for at least a week for better data coverage?

Please clarify.

Response: We apologize for the confusion caused by our inappropriate description.

Our observations lasted 30 days. The O₃ pollution lasted for 10 days from June 8 to 17, and for 8 days from June 20 to 27. As you said, for better data coverage, we only discussed periods of O₃ pollution that lasted at least a week, and processes with relatively few days of pollution were not discussed. In the manuscript, we have also made modifications accordingly. (Line 210-212)

Line 210-212: Meanwhile, there were also O₃ pollution events on 6th Jun. and 29th-30th Jun. However, for better data coverage, we only discussed periods of O₃ pollution that lasted at least a week, and processes with relatively few days of pollution were not discussed in this study.

224 This is a very large proportion of halocarbons. It would be really interesting to see which VOCs are included in each category in your study, and what the average mixing ratios were across the sampling period. Please include this as an expanded version of Table 1 in the supplementary.

Response: Thank you for this very thoughtful suggestion. We have shown all the observed NMVOCs and their related statistics in

Table S1.

231 Remove “if”.

Response: Thanks for the suggestion. It has been deleted.

236 Explain what you mean by the “top fifteen VOC species”. Do you mean the highest average mixing ratio? If so, please replace “top” with something like “the fifteen VOCs with the highest average mixing ratio across the observation period.”

Response: Sorry for this mistake.

What we mean is the 15 NMVOCs with the highest average mixing ratio across the observation period. According to your request, we have replaced the “Comparisons of the top fifteen NMVOCs during different processes, ppbv. Error bars are standard deviations.” to “Comparisons of the fifteen NMVOCs with the highest average mixing ratio during different processes, ppbv. Error bars are standard deviations”. (Line 293-294).

Line 293-294: **Figure 2.** Comparisons of the fifteen NMVOCs with the highest average mixing ratio during different processes, ppbv. Error bars are standard deviations.

253 “As illustrated in the following PMF source apportionment”.

Where is this? I cannot see any source apportionment in this section,

just some discussion of the possible sources of different VOCs from the literature.

Response: We apologize for the confusion caused by our inappropriate description.

Here our preliminary analysis found that vehicle exhaust, solvent use, combustion, biogenic emission, and industrial processes are important sources of NMVOCs at observation sites. In section 3.2.2, we used PMF to analyze the sources of NMVOCs and reached a similar conclusion. We try to express that the analysis here is consistent with the analysis in section 3.2.2.

Therefore, we have replaced the “as also illustrated in the following PMF source apportionment.” to “as also illustrated in the following PMF source apportionment (in section 3.2.2)”. (Line 289-291).

Line 289-291: Therefore, vehicle exhaust, solvent use, combustion, biogenic emission, and industrial processes are important sources of NMVOCs at observation sites, as also illustrated in the following PMF source apportionment (in section 3.2.2).

255 I don't understand what Figure 2 shows. What does the line represent and what are the bars? What are the authors trying to say using this figure?

Response: Thank you for your feedback.

In our study, the bars in Fig. 2 represent the concentration of each species, while the line represents the cumulative percentage of each species' concentration in the total volatile organic compounds (TNMVOCs) concentration. One of our aims is to show the top fifteen substances by concentration, as they have high concentrations and large percentages, making them key substances of interest. Additionally, by calculating the percentage of the top 15 NMVOCs in TNMVOCs, we aim to express the importance of these NMVOCs.

260 “Major” VOCs – why exactly were these selected? You could either just say “a selection of VOCs”, or if you are pointing out that these are the major ones, you need to explain why.

Response: Thanks for the suggestion.

We have replaced the “Major VOCs” to “A selection of NMVOCs”.
(Line 298).

Line 298: A selection of NMVOCs, O₃, and NO_x were selected, and their daily changes were analyzed, as shown in Fig. S4.

264 “photochemical reaction” – change to “photochemical reactivity”, as there are multiple photochemical reactions happening.

Response: Thanks for the suggestion.

We have replaced the “photochemical reaction” to “photochemical reactivity”. (Line 302 and Line 305).

Line 302: Higher O₃ production during the day indicates a strong photochemical reactivity.

Line 305: This is associated with a higher boundary layer and strong photochemical reactivity during the day.

271 Explain what you mean by “the daily change was consistent with NO_x”.

Response: Thanks for the suggestion.

As shown in Fig. S4 of supplementary materials, the concentrations of ethane, propane, butane, pentane, ethylene, propylene, benzene, and toluene exhibit a bimodal diurnal pattern. Similarly, the diurnal variation of NO_x concentration also displays a bimodal trend. Furthermore, the peak times of these NMVOCs and NO_x concentrations align relatively closely. Therefore, in line 276, we state, 'Additionally, the peak concentrations of these NMVOCs occur in the morning and evening (7:00-8:00 and 23:00-24:00), showing a consistent daily pattern with NO_x.

We have carefully considered your suggestion and have made the necessary revisions in the manuscript. Specifically, we have amended the sentence as follows: In addition, the peak

concentrations of these NMVOCs were observed in the morning and evening (7:00-8:00 and 23:00-24:00), showing a consistent daily pattern with NO_x. This suggests that the emissions of these NMVOCs are significantly influenced by motor vehicle emissions and fuel combustion. (Line 307-309)

Line 307-309: In addition, the peak concentrations of these NMVOCs were observed in the morning and evening (7:00-8:00 and 23:00-24:00), showing a consistent daily pattern with NO_x.

273 What are “traditional nighttime activities”?

Response: Thanks for the suggestion.

In this context, the "traditional nocturnal activities of the city" refer to the typical or customary activities that take place at night. This could include increased traffic from people eating out, attending events or socializing. At the same time, due to the restrictions on large trucks during the day, many large trucks will travel intensively at night, resulting in higher levels of NMVOCs and NO_x emissions.

279 Acetone is a “common VOC” – what does this mean? Consider changing the language.

Response: Sorry for the mistake.

We have replaced the “Acetone is a common NMVOCs and comes

from a wide range of sources” to “Acetone comes from a wide range of sources”. (Line 318).

Line 318: Acetone comes from a wide range of sources, mainly from vehicle emissions, industrial production, and secondary formation.

297 Could it be that the pentanes come from a mix of sources? The text implies that for Case 1, Case 2 and clean days, the sources are exclusively NG emissions, Vehicular exhaust emissions, and liquid gasoline emissions respectively.

Response: Thanks for the suggestion.

Yes, it is possible that the pentanes come from a mix of sources. For example, pentanes can also be found in industrial emissions, evaporative emissions from fuel storage and handling, as well as natural sources such as vegetation and wildfires.

However, previous studies have tended to preliminarily determine the emission source of pentanes by calculating the ratios of isopentane/n-pentane. There are some differences in values of isopentane/n-pentane among natural gas emissions (NG, 0.8-0.9), vehicle emissions (2.2-3.8), liquid gasoline (1.5-3.0), and fuel evaporation (1.8-4.6) (Gilman et al., 2013;McGaughey et al., 2004;Watson et al., 2001). Therefore, the ratio method was used in

this study to calculate the ratios of isopentane/n-pentane, so as to preliminarily determine the source of pentane.

In this study, the ratios of Case 1, Case 2, and clean days were 0.7, 2.5, and 1.1, respectively. It suggests that isopentane and n-pentane may come from NG emissions, vehicular exhaust, and liquid gasoline, respectively.

- 311 Was this value 0.5 for all three cases? How does this ratio vary with wind speed? Perhaps this could further support the argument of E/X ratios indicating that air masses were affected by transport?

Response: Thank you for your valuable suggestion.

Yes, in our study, this ratio was 0.5 for all three cases. Exploring the relationship between wind speed and the E/X ratios can provide additional evidence supporting our argument that air masses were influenced by transport. According to your requirements, we have analyzed the relationship between ethylbenzene, m/p-Xylene, E/X, and wind direction and speed. As shown in Fig. S5, the concentrations of ethylbenzene and m/p-Xylene are mainly influenced by winds coming from the northwest, and their concentrations tend to increase with stronger wind speeds. Similarly, E/X also exhibits similar patterns of variation. This further indicates that the regional transport of ethylbenzene and

m/p-Xylene from distant sources. We have included this analysis in our revised manuscript to strengthen our conclusions. (Line 351-354)

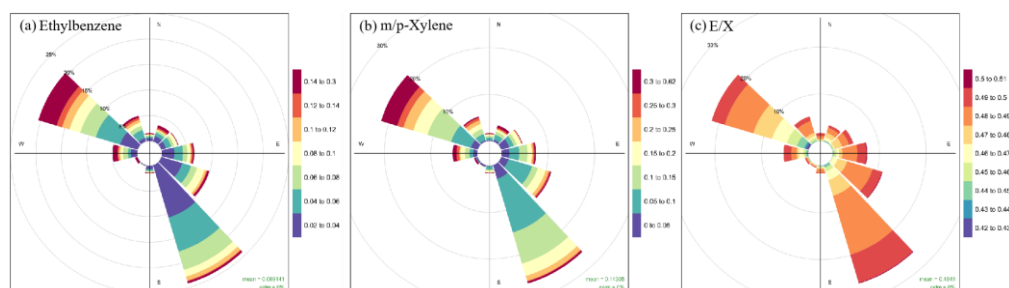


Figure S5. The rose diagrams of transport contributions from polluted sources for Ethylbenzene and m/p-Xylene which locate indifferent directions.

Line 351-354: As shown in Fig. S5, the concentrations of ethylbenzene and m/p-Xylene are mainly influenced by winds coming from the northwest, and their concentrations tend to increase with stronger wind speeds. Similarly, E/X also exhibits similar patterns of variation. This further indicates that the regional transport of ethylbenzene and m/p-Xylene from distant sources.

315 Generally for this section, more discussion of the potential locations of some of these sources would be good to see. There are two solvent factors. Why is this? Different industrial sources? Are there any industrial sources in the northeast and southeast of the site? For factor 7, are there any industrial sites near the observation site? Are the source apportionment factors consistent with the

geography of the site?

Response: Thank you for your comments.

In fact, we tried solutions with different factors. As shown in Fig. S2, we explored the number of PMF factors from 3 to 12 to obtain the best solution. Each model is run 20 times. The values of $Q_{\text{true}}/Q_{\text{expected}}$ in different solutions are discussed subsequently. F_{peak} values from -2 to 2 are used in the model. We find that when the number of factors increases from 3 to 7, the change in the values of $Q_{\text{true}}/Q_{\text{expected}}$ is relatively stable. However, when the number of factors is increased to 8, the values of $Q_{\text{true}}/Q_{\text{expected}}$ fluctuate significantly. We also find that when F_{peak} is 0, the values of $Q_{\text{true}}/Q_{\text{expected}}$ are lowest. Finally, we adopted a 7-factor solution ($Q_{\text{true}}/Q_{\text{expected}} = 3.42$; and $F_{\text{peak}} = 0$). Therefore, choosing 7-factor solution is the most appropriate choice.

However, we found that substances contributing significantly to Factor 6 and Factor 7 are often used as organic solvents. We also consulted the literature and found similar occurrences in previous studies. Xu et al. (2023) used the PMF model to analyze the main sources of NMVOCs in the Yangtze River Delta region and identified two solvent usage sources. It is worth noting that the key contributing species in the two solvent usage sources in the Yangtze

River Delta region are quite consistent with our study. In their research, factor 3 and factor 6 were determined as solvent usage-toluene and solvent usage-C8 aromatics, respectively. Factor 3 was characterized by C5-C7 alkanes and toluene, while factor 6 was characterized by ethylbenzene, m/p-xylene, and o-xylene. As shown in Fig. 4 of our study, factor 6 and factor 7 were identified as solvent usage 1 and solvent usage 2. Factor 6 was characterized by chloromethane, dichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, and ethyl acetate. Although these species did not appear in Wang et al.'s study, it is evident that these substances are common organic solvents in industrial applications. Factor 7 was characterized by a high percentage of methylcyclopentane, cyclohexane, TEXs (Toluene, Ethylbenzene, m/p- Xylene, and o-Xylene), 1,2-Dichloroethane, 1,2-Dichloropropane, and Ethyl acetate. As we know, TEXs are related to the use of solvent cleaners in coatings, paintings, synthetic fragrances, adhesives, and solvents (Zhang et al., 2021). 1,2-Dichloroethane, 1,2-Dichloropropane, and Ethyl acetate are also commonly used scientific chemical reagents.

In addition, other studies by various scholars have also identified two solvent usage sources (Zhang et al., 2023; Wang et al., 2020; Song et al., 2019; Lyu et al., 2016).

Figure 1 shows the distribution of industrial sites around the observation points. It can be seen that there are a large number of industrial sites in Zhengzhou city. There are many industrial productions to the southeast and northeast of the observation points. We also found that there are indeed industrial facilities around Factor 7. We have carefully evaluated the source apportionment factors and believe that they are consistent with the geographical characteristics of the study site.

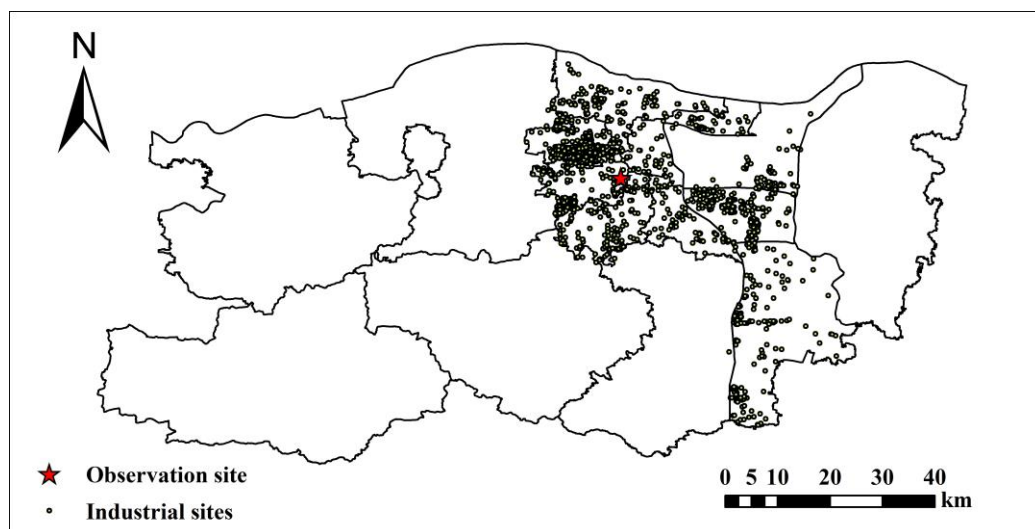


Figure 1. Distribution of industrial sites around observation sites.

369 This is really interesting. Are you saying that O₃ pollution events appear to be independent of the VOC sources, and these remain broadly similar? If this is the case, then what is driving these O₃ pollution events. Is it the meteorology? Please explain this in the manuscript

Response: Thank you for your comments.

In this study, the contributions of various pollution sources show relatively minor differences between O₃ pollution events and clean days, but there are still some distinctions. For instance, compared to clean days, in Case 1 events, industrial production, biogenic emission, LPG/Ng, and solvent usage increased by 2%, 3%, 2%, and 2% respectively. Compared to clean days, in Case 2 events, solvent usage, biogenic emission, and LPG/Ng increased by 3%, 5%, and 16% respectively. Therefore, the increased contributions of solvent usage, biogenic emission, and LPG/Ng may have a certain impact on the formation of O₃ pollution.

The reasons for O₃ formation in the area may involve various complex factors, including but not limited to emissions of nitrogen oxides, levels of solar radiation, meteorological conditions, etc.

First, we compared the average concentrations of nitrogen oxides in Case 1, Case 2, and clean days. The average concentrations of NO₂ in Case 1, Case 2, and clean days were 27.4 ± 19.5 , 24.9 ± 12.3 , and 24.4 ± 16.1 ppbv, respectively, while the average concentrations of NO were 3.9 ± 3.6 , 3.9 ± 2.4 , and 4.8 ± 5.5 ppbv, respectively. The average concentrations of NO₂ in pollution events were higher than those in clean days, while the average concentrations of NO were lower than those in clean days. Higher concentration of NO₂ can promote the formation of O₃, while the

titration reaction between NO and O₃ consumes O₃ (Sillman, 1999). Therefore, the higher concentration of NO₂ and lower concentration of NO during pollution events are one of the reasons for the occurrence of O₃ pollution events.

Second, we further explored the relationship between meteorology and O₃ concentration. According to Fig. S3a and Fig. S3b, it can be observed that O₃ concentration shows a linear increasing trend with temperature and a linear decreasing trend with RH. O₃ has a significant correlation with temperature and RH, with correlation coefficients of 0.7 and -0.61 respectively. Therefore, conditions of high temperature and low RH are more conducive to O₃ pollution. Figure S3c indicates that O₃ concentration exceeding the secondary standard mainly occurs under meteorological conditions of high temperature (greater than 30 °C) and low RH (less than 55%). It can be noted that when 35 °C < T < 40 °C and 20% < RH < 40%, the O₃ concentration consistently exceeds the secondary standard. Meng et al. (2023) argued that most of the reactions involved in O₃ formation increase with temperature, and the rate of O₃ production exceeds that of O₃ loss by a large margin.

In conclusion, in addition to the impact of solvent usage, biogenic emission, and LPG/NG on O₃ pollution events, meteorological

factors are also significant factors in the occurrence of O₃ pollution events.

In addition, we have added an analysis of the correlation between O₃ and temperature and RH in the manuscript. (Line 235-253)

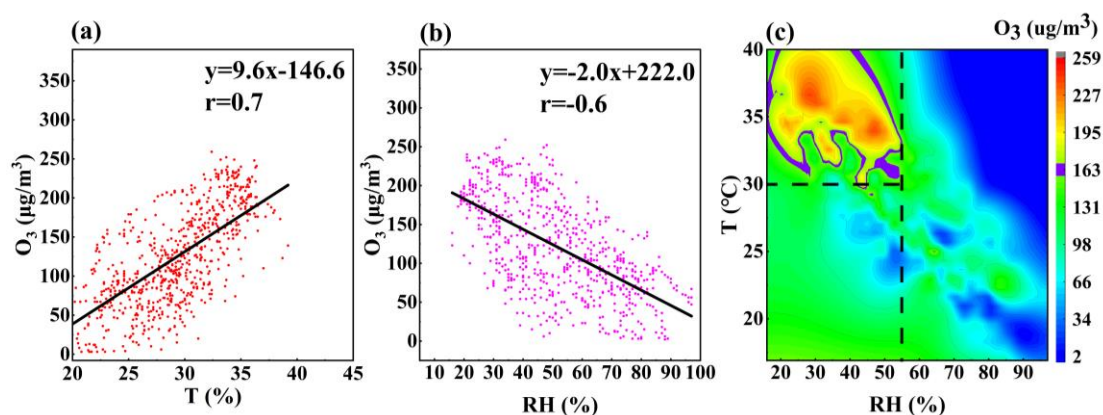


Figure S3. Correlation analysis of O₃, T, and RH.

Line 235-253: The average concentrations of TNMVOCs, NO₂, PM₁₀, and PM_{2.5} on clean days were lower than those of the O₃ pollution events. The average RH ($65 \pm 17\%$) on clean days was higher than those during Case 1 and Case 2 events, while the average temperature ($26.0 \pm 4.8^{\circ}\text{C}$) was lower than those during Case 1 and Case 2 events. According to the analysis in Fig. S3a and Fig. S3b, O₃ has a significant correlation with temperature and RH, with correlation coefficients of 0.7 and -0.61 respectively. Therefore, conditions of high temperature and low RH are more conducive to O₃ pollution. Fig. S3c indicates that O₃ concentration exceeding the secondary standard mainly occurs under meteorological conditions of high temperature (greater than 30 $^{\circ}\text{C}$)

and low RH (less than 55%). It can be noted that when $35\text{ }^{\circ}\text{C} < T < 40\text{ }^{\circ}\text{C}$ and $20\% < \text{RH} < 40\%$, the O_3 concentration consistently exceeds the grade II threshold of the NAAQS-2012. High temperature and low RH are more conducive to O_3 pollution (Chen et al., 2020; Zhang et al., 2015). Meng et al. (2023) argued that most of the reactions involved in O_3 formation increase with temperature, and the rate of O_3 production exceeds that of O_3 loss by a large margin. Therefore, during the study period, the meteorological conditions of high temperature and low RH are also important factors affecting the occurrence of O_3 pollution.

Besides, the average concentration of NO_2 in clean days (24.4 ± 16.1 ppbv) was lower than that in Case 1 and Case 2, while the average concentration of NO in clean days (4.8 ± 5.5 ppbv) was higher than that in Case 1 (3.9 ± 3.75 ppbv) and Case 2 (3.9 ± 2.4 ppbv). Higher concentration of NO_2 can promote the formation of O_3 , while the titration reaction between NO and O_3 consumes O_3 (Sillman, 1999). Therefore, the higher concentration of NO_2 and lower concentration of NO during pollution events are one of the reasons for the occurrence of O_3 pollution events.

383 This is the wrong way around - O_3 formation was more sensitive to biogenic emissions, not “biogenic emission was more sensitive to O_3 formation”.

Response: Sorry for this mistake.

We have replaced the “indicating that biogenic emission was more sensitive to O₃ formation” to “indicating that O₃ formation was more sensitive to biogenic emissions”. (Line 451-452).

Line 451-452: During the entire period, especially in the pollution events, the RIR of AVOCs was lower than that of BVOCs, indicating that O₃ formation was more sensitive to biogenic emissions.

385 From Fig. 6, the RIRs look broadly similar between Case 1, Case 2, and clean. In the text, the authors have suggested there is a difference between clean and polluted days. Could you please quantify what this difference is? For example, what is the percentage difference in RIRs during polluted days, and is this significant?

Response: We appreciate the reviewer's insightful feedback.

As you pointed out, the RIRs appear broadly similar between Case 1, Case 2, and clean days. Due to the focus of this study on the summer month of June, characterized by strong sunlight, high temperatures, and low RH, conditions were highly conducive to photochemical reactions. As introduced in section 3.1.1, the concentrations of TNMVOCs during pollution events and clean

days were relatively low and showed minimal variations. Additionally, there were no significant changes in temperature and RH. Therefore, when analyzing O₃ sensitivity, the RIR values of various species in each process are relatively close, and the percentage differences in RIRs were not significant.

To address the difference between clean and polluted days in terms of RIRs, we have quantified this in detail. The percentage difference in RIRs during polluted days compared to clean days has been calculated. More analysis has been provided in the revised manuscript to clarify this aspect more effectively. (Line 446-448)

Line 446-448: Compared to clean days, the RIR value of AVOCs decreased by 11%, with Aromatics showing the largest decrease (26%), while Alkanes and Alkenes increased by 7% and 3% respectively. In pollution events, CO and NO_x were reduced by 29% and 22%, respectively.

408 Please clarify which data you have used to generate the Isopleth in Fig. 7. Have you used the average peak O₃ across the entire observation period? Or is this the average daytime O₃ between particular hours? There is a point for “base case”, but it would be interesting to see where Case 1, Case 2 and clean days would appear on this isopleth.

Response: We appreciate the reviewer's feedback.

Firstly, in OBM, we designed a total of 36 sets of simulated scenarios. The concentration of AVOCs decreases in 20% increments, as does the concentration of NO_x. In the Isopleth plot, the 'base case' represents scenarios where the concentrations of AVOCs and NO_x are not reduced. The horizontal and vertical axes represent the proportions of the concentrations of AVOCs and NO_x to their concentrations in the unreduced state, respectively. The isopleth represents the average O₃ concentration over the entire observation period. The isopleth represents the average O₃ concentration from 10 a.m. to 4 p.m. each day throughout the entire observation period. To create the O₃ EKMA curve, the data points of the maximum O₃ concentration generated by simulation between 10:00 and 16:00 are linearly fitted into colored surfaces. The data points of the same color on the colored surface are then connected to form the O₃ EKMA curve.

To see the positions of Case 1, Case 2, and clean days on the isopleth, we have redrawn an EKMA curve (Fig. S7). The horizontal and vertical axes represent AVOCs and NO_x concentrations under different reduction scenarios, respectively, while the isopleth indicates the maximum O₃ concentration value in each scenario group. We have replaced Fig. 7 in the manuscript.

As can be seen from the Fig. 7, Case 1, Case 2, and clean days are all above the ridge line, indicating that the two pollution events and clean days are all in the AVOCs control area.

we have provided additional information on the positions of Case 1, Case 2, and clean days on the isopleth in the revised version of the manuscript. Thank you for highlighting this point. (Line 483-485)

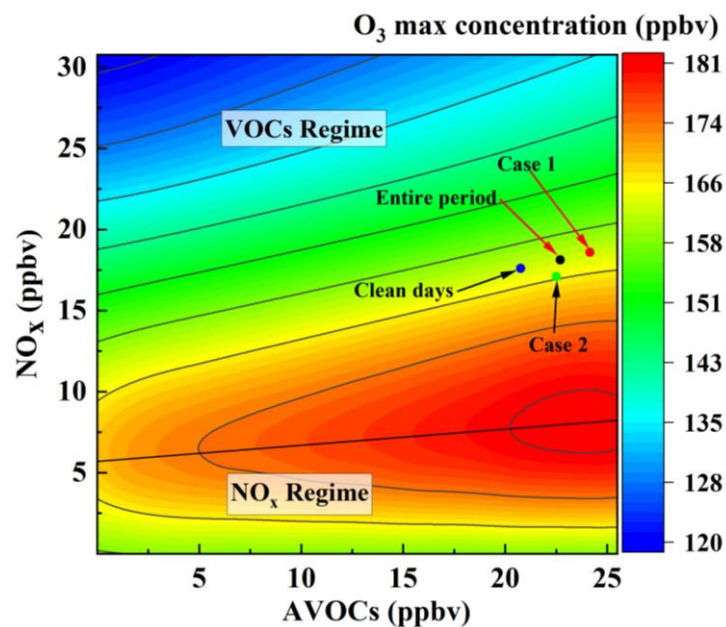


Figure S7. EKMA curves of the O₃ max concentration.

Line 483-485: At the same time, Case 1, Case 2, and clean days are all above the ridgeline and belong to the AVOCs control region (Fig. S7). Therefore, reducing AVOCs can effectively reduce the generation of O₃.

451 This seems quite general, after the detail you have gone into earlier on the RIRs for VOC groups and looking closely at different

sources. I understand why biogenic compounds have not been included, but the impact of these should be further acknowledged in the text as changes to biogenic emissions present a large uncertainty to how O₃ production might change in the future. It would have been interesting to see how O₃ production might change when the different sources are reduced alongside NO_x. This is more useful to policy than just investigating different percentage changes in bulk AVOCs, as it would be challenging to reduce AVOC emissions in this way.

Response: Thanks for the valuable suggestion.

In section 3.3.1 of the manuscript, we have further acknowledged the impact of biogenic emissions on O₃ production. Through comparisons with studies from other cities, we have also observed the significance of biogenic emissions on urban O₃ production. (Line 449-459).

We acknowledge the importance of exploring the effects of reducing emissions from different sources in conjunction with nitrogen oxides on O₃ production. While we recognize the significance of this investigation, we agree that our current manuscript does not provide a clear and sufficient exploration of this aspect. Therefore, we plan to further elaborate on this topic in

future research to address your valuable suggestion.

Line 446-459: Isoprene was the sole BVOC considered in this study. Isoprene is an important tracer to indicate biogenic emissions (Xie et al., 2021; Li et al., 2024; Qin et al., 2023). During the entire period, especially in the pollution events, the RIR of AVOCs was lower than that of BVOCs, indicating that O₃ formation was more sensitive to biogenic emissions. This may be due to increased emissions of BVOCs at higher temperatures and solar radiation conditions, as well as their high reactivity and O₃ formation potential. Studies in Yucheng (Zong et al., 2018), Leshan (Xie et al., 2021), and Nanjing (Fan et al., 2021; Ming et al., 2020) have shown that O₃ is highly sensitive to BVOCs. Studies in Zhengzhou (Wang et al., 2022), Hangzhou (Zhao et al., 2020), and Hong Kong (Wang et al., 2017) suggested that O₃ exhibits greater sensitivity to BVOCs than AVOCs during hot seasons. Wang et al. (2019) found in their study on O₃ source apportionment in Henan Province, where Zhengzhou is located, that BVOCs contribute to approximately 23.9% of the O₃ attributed to NMVOCs. Therefore, the contribution of BVOCs to O₃ is very important.

441 You say P(O₃) increases respectively, but what is this respective to?
Is this per hour?

Response: We apologize for the confusion caused by our inappropriate description.

First, we modified the term 'P(O₃)' to 'O₃ concentration' to represent the change in O₃ concentration with the reduction of AVOCs and NO_x emissions. We also adjusted the vertical axes in Fig. 8 and Fig. S8.

Second, we have replaced the “In this case, P(O₃) increases by 30, 21, 16, 13, 13, 15, and 15% respectively” to “In this case, O₃ concentration increased by 30, 21, 16, 13, 13, 15, and 15% from 10 a.m. to 4 p.m.”. (Line 519).

Line 519: In this case, O₃ concentration increased by 30, 21, 16, 13, 13, 15, and 15% from 10 a.m. to 4 p.m.

453 The authors could work on bringing all of these results together in the conclusion, rather than just summarising the key result of each section in turn. What is driving O₃ production? Is it related to sources? Is it the meteorology?

Response: Thank you for the valuable feedback on our study.

In the revised manuscript, we have integrated all results in the conclusion section, rather than just summarizing the key findings of each section separately. we have enhanced the discussion in the revised manuscript to elucidate the interplay between O₃

production and meteorological conditions. Finally, we found that the occurrence of O₃ pollution processes is related to the increase of pollutant concentration, the change of emission sources, and adverse meteorological factors. These revisions aim to provide a more thorough understanding of the mechanisms governing O₃ production. (Line 532-551)

Line 532-551: The summer O₃ pollution has always been an important environmental issue in Zhengzhou. This study investigated the characteristics and emission sources of O₃ precursors from 1st to 30th June 2023. The OBM was used to analyze the influence of precursors on the formation of O₃, and the emission reduction strategy of precursors was proposed to control the concentration of O₃. During the entire period, the concentration of TNMVOCs varied from 9.9 to 60.3 ppbv, with an average value of 22.9 ± 8.3 ppbv. The average concentration of TNMVOCs during O₃ pollution was higher than that during clean days. Alkanes (44%), OVOCs (20%), and halocarbons (19%) were the most abundant NMVOCs group. Ethane, acetone, and propane were always the most abundant species. The average concentrations of NO₂ in pollution events were higher than those in clean days, while the average concentrations of NO were lower than those in clean days. Therefore, the increasing concentration of O₃ precursors is

one of the reasons for the formation of O₃ pollution. At the same time, the unfavorable meteorological conditions of high temperature and low RH in the observation process are also important factors in the formation of O₃ pollution. Further analysis of the source of these precursors found that Vehicular exhaust (28%), solvent usage (27%), and industrial production (22%) were the main emission sources of NMVOCs. The increase of solvent usage, biogenic emission and LPN/NG contribution is an important cause of O₃ pollution. Sensitivity analysis of O₃ to precursors found that NMVOCs had the highest RIR value, while NO_x had a negative RIR value. Alkenes have the highest RIR value among AVOCs. It should be noted that the RIR value of BVOCs was greater than that of AVOCs. The local O₃ formations were in the AVOCs-limited regimes, which means reducing the concentration of AVOCs was an effective way to reduce O₃ concentration. Meanwhile, we suggest that the minimum reduction ratio of AVOCs/NO_x should be no less than 3:1 to reduce O₃ production.

465 Olefins mentioned here, earlier referred to as alkenes. Please change to alkenes.

Response: Sorry for this mistake.

It has been corrected.

Reference:

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