Referee comments：

The study investigates the characteristics of VOCs and their importance in ozone formation during June in Zhengzhou City, China. The study focuses on the interesting relationship of O_3-NO_x-VOCs during summer, which is crucial for ozone control strategies. The study compares O_3 pollution events and clean days regarding different sources and O_3 formation sensitivity. However, the manuscript is poorly written and not up to the mark for consideration for publication in ACP. The authors fail to discuss crucial sections of the manuscript.

The authors do not include basic details about the instrumentation and dataset. Why is only a small part of the VOC measurement included in the PMF analysis? The reason is not mentioned properly in the manuscript or supplementary.

More in-depth comparisons with similar previous studies in Chinese/ Zhengzhou city would enhance the wider impact of the manuscript. Details about common factors and key trace VOC species can also be included. Any new or unique source or marker emerging from the region during the study may provide valuable insights.

Discussion related to the influence of meteorology and the transport of air masses needs to be included and explained.

Some of the statements require supporting references and proper reasoning.

Also, VOCs can be changed to NMVOCs throughout the manuscript.

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 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.

Detailed comments:

Lines 114-115: "The sampling site is surrounded by residential areas, commercial areas, and office buildings, and there are no obvious atmospheric pollution sources nearby, which is a typical urban site.". These lines should be changed to the following for better clarity. "The sampling site is a typical urban site, surrounded by residential areas, commercial areas, and office buildings. There are no point sources of air pollution nearby (mention up to how much radius)."

Response: Thanks for the suggestion.

We appreciate your suggestion to improve the clarity of the description of the sampling site. We have revised the relevant lines as per your recommendation:

"The sampling site is a typical urban site, surrounded by residential areas, commercial areas, and office buildings. There are no point sources of air pollution nearby within a radius of 1 meter."

We believe that these changes enhance the clarity of the description and provide a more precise understanding of the sampling site.

We have revised the manuscript according to your request. (Line 112-114)

Line 112-114: The sampling site is a typical urban site, surrounded by residential areas, commercial areas, and office buildings. There are no point sources of air pollution nearby within a radius of 1 meter.

Line 99 'heaviest' should be 'highest'

Response: Sorry for this mistake.

We have replaced the "heaviest" to "highest".

Lines 116-117: "The sampling site is surrounded by roads and vegetation, and the sampling may be affected by motor vehicle emissions and

plant emissions." changed to "The sampling site may be affected by motor vehicle and plant emissions."

Response: Thanks for the suggestion.

We have revised the original content according to your request. (Line 115)

Line 115: The sampling site may be affected by motor vehicle and plant emissions.

Section 2.2. Sample collection and chemical analysis

More details should be provided about the instruments used for supporting measurements. Details about the input of sampling air should be added. Details about sampling dates, calibration, sampling time resolution, etc, should be added.

Response: Thanks for the suggestion.

As per your request, we have added some more details about the instrument. (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 H_2O_2 and CO_2. 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).

Section 2.3 PMF model

Only 29 out of 115 VOCs have been used for PMF analysis. Why is that? Multiple studies have used more than ~90 VOCs in the PMF model and shown its advantages. The author mentioned that species with missing samples were excluded. A very high proportion of sampling is missed out. This questions the reliability of the collected samples and dataset. More details about the error matrix and uncertainty should be included in this section. Why were the 5-factor solution, 6-factor solution, and 8- factor solution not considered? Did the author observe any source tracers or markers mixing in these solutions?

Response: Thanks for the useful comment and constructive

suggestions. The introduction was reorganized to make it clearer. Next, we will respond to the above questions one by one.

1. First, we chose to analyze 29 out of 115 NMVOCs for PMF analysis based on the specific objectives and data collection methods of our study. Some NMVOCs were excluded due to missing samples, as we aimed to ensure the accuracy and reliability of the data. Second, our research followed three principles in selecting species: (1) species with relatively high proportions of samples missing or with concentration values more than 25% below the MDLs were excluded; (2) typical NMVOCs tracers of emission sources were included; (3) NMVOCs with short atmospheric lifetimes were excluded.

2. We searched the literature and indeed found that some studies have used more than 90 types of NMVOCs in PMF software. Wang et al. and Jain et al. used PMF software to analyze over 90 NMVOCs in the Delhi. Wang et al. analyzed 101 NMVOCs in the Beijing. In Li et al. (2022) 's study, a total of 225 chemicals were used in the PMF model to quantitatively analyze the contribution of possible sources of NMVOCs measurements during CTT movement. However, these studies mention that PMF analysis uses more than 90 ions as an input matrix to identify different emission sources. These studies used ions, not NMVOCs. In addition, we also read some recent literature studies and found that some studies still use less than 50 NMVOCs (Yu et al.,

2022;Pernov et al., 2021;Mishra et al., 2023;Zhang et al., 2023;Zuo et al., 2024). We acknowledge the advantages of using a larger range of volatile organic compounds for PMF model analysis in the study. In future research, we will consider expanding the scope of NMVOCs to gain a more comprehensive understanding of the sources and impacts of air pollutants.

3. 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 Q_{robust}, Q_{true} , $Q_{theoretical}$, Q_{true}/Q_{robust} , and Q true / Q theoretical in different solutions are discussed subsequently. Fpeak values from −2 to 2 are used in the model. Finally, we adopted a 7-factor solution ($Q_{true}/Q_{theoretical}$ = 3.42; and Fpeak = 0). In addition, we also add some explanations about the rational selection of factors in the manuscript.

4. The emission sources of NMVOCs in the atmosphere are complex, and different sources may emit the same substances. Therefore, when using the Positive Matrix Factorization (PMF) software for source apportionment analysis, different sources may have common substances. However, each source has unique tracer substances. Currently, most studies identify different sources based on characteristic substances. In this study, typical tracer substances used for solvent sources include chloromethane, dichloromethane,

tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, ethyl acetate, methylcyclopentane, cyclohexane, TEXs (Toluene, Ethylbenzene, m/p-Xylene, and o-Xylene), 1,2-Dichloroethane, 1,2-Dichloropropane, and Ethyl acetate. Methylcyclopentane and cyclohexane. These substances are commonly used in solvent applications. In solvent sources, we also observed some other substances that cannot be used as solvents. We have reviewed many literatures and found similar issues. However, the proportion of these substances in this factor is very small, so they can be ignored.

Section 2.4 Conditional bivariate probability function analysis

More details in the section are required.

Response: Thank you for your valuable feedback.

Regarding Section 2.4, we have acknowledged the error in the title "Conditional bivariate probability function analysis" and have made the necessary correction to "Conditional probability function analysis" in the manuscript. Additional details have been included to provide a more comprehensive explanation of the content in this section. We have aimed to enhance the clarity and understanding of our study for the readers. Thank you for guiding us in improving our manuscript.

Line 192 areas are non-polluting processes (clean days). Remove 'non-polluting processes'

Response: Thanks for the suggestion. We have revised the text to remove the phrase "non-polluting processes".

Line 192-193 During the observation, O_3 polluted days were 22 days, accounting for 73%. You mentioned cases 1 (8th-17th Jun.) and 2 (20th-27th Jun.) as pollution events, which is 18 days instead of 22 days. There is a discrepancy. Most of the days are included in ozone pollution events in June.

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

1. As mentioned in line 197, during the entire observation process, apart from Cases 1 (8^{th}-17^{th} Jun.) and Case 2 (20^{th}-27^{th} Jun.), O_3 pollution also occurred on 6th Jun. and 29^{th}-30^{th} Jun. O_3 pollution lasted a total of 18 days during Cases 1 and Case 2, but throughout the observation process, O_3 pollution occurred for a total of 21 days.

2. We apologize for the discrepancy in the statistical methods, where the manuscript originally stated "22 days." We have now corrected it to "21 days."

3. We have modified the "During the observation, O_3 polluted days were 22 days, accounting for 73%." to "During the observation, O_3

polluted days were 21 days, accounting for 70%". (Line 215-216)

Line 215-216: During the observation, O_3 polluted days were 21 days, accounting for 70%.

Line 198 'The mean concentrations' change to 'The daily mean concentrations'.

Response: Thanks for the suggestion.

We actually use the hourly average concentration. We have replaced "The mean concentrations" to "hourly average concentration". (Line 221-222).

Line 221-222: Hourly average concentration of SO_2, NO_2, CO, and $PM_{2.5}$ were 4.4 ± 3.3 μg/m^3, 26.5 ± 17.9 μg/m^3, 0.6 ± 0.2 mg/m^3, 59.6 ± 26.5 μg/m^3 and 22.9 ± 7.1 μg/m^3, respectively.

199-200: All were lower than the ambient air quality standard value (National or WHO). Add reference. Also, compare the values with national standards/ WHO standards for pollutant criteria.

The mean of each VOCs species (115 in number) or at least which species have been measured should be added to the supplementary in Table.

The variation of different families or groups of VOCs can be added as a time series in Figure 1. Also, the left and right y-axis are not aligned properly with the text.

Response: Thank you for providing valuable feedback. We apologize for this unclear illustration. We have carefully considered your suggestions and made the necessary revisions. Below are our responses to each of the points you raised:

1. We added comparisons of pollutant concentrations with the grade I threshold of the China National Ambient Air Quality Standard (NAAQS-2012) to our manuscript. We have modified the "All of them were lower than the ambient air quality standard value." to "The concentrations of these pollutants were 97%, 87%, 94%, and 35% lower than the grade I threshold of the NAAQS-2012". (Line 222-223).
2. We have added the mean concentration of each of the 115 NMVOCs species that have been measured to the supplementary Table S1 in Supplementary materials.
3. The variation of different groups of NMVOCs has been included as a time series in Figure 1.
4. The alignment of the left and right y-axes with the text has been adjusted to ensure clarity and accuracy of the figures.

Line 222-223: The concentrations of these pollutants were 97%, 87%, 94%, and 35% lower than the grade I threshold of the NAAQS-2012.

Section 3.2 Sources of VOCs

Figure 4: The VOCs concentration is given in ug/m^3, while it is mentioned as ppbv in the whole manuscript. Please check the discrepancy in the units.

An explanation of each factor concerning the sampling site is required. As you mentioned, there are no point sources nearby, so why is industrial pollution showing 22%? What could be the contributing factors for it?

Have you also performed PMF on clean days and polluted days simultaneously? One suggestion is to check if PMF gives different results in different cases (Case 1 and Case 2 and clean days) and compare the results.

Secondary VOCs, such as OVOCs and amines, play an important role in identifying VOCs sources. The ratio of OVOCs and other family groups should also be analysed in each source to determine their contribution. This will give great insights into the source characterisation.

Response: Thank you for valuable suggestions. Below are our responses to each of the points you raised:

1. We apologize for the mistake in Figure 4 where the NMVOCs concentration is incorrectly labeled as μg/m^3 instead of ppbv. We will correct this error in the revised manuscript. The correct unit for

NMVOCs concentration in Figure 4 should indeed be ppbv, consistent with the rest of the manuscript.

2. There are indeed no large industrial emission sources near the monitoring site, but the industrial emissions in Zhengzhou city account for a very high proportion. Lu et al. (2024) analyzed the NMVOCs emission inventory of Zhengzhou city in their latest study, and combined with the PMF model to analyze the sources of NMVOCs. Both the NMVOCs emission inventory and PMF simulation results indicate that Zhengzhou is heavily influenced by industrial sources. Liu et al. (2024) established a NMVOCs emission inventory for the Central China region represented by Henan Province. The inventory shows that Zhengzhou is the city with the largest NMVOCs emissions, and industrial emissions are the main contributing source of NMVOCs. Therefore, although there are no large industrial emission sources near the monitoring site, due to the large industrial emissions in the Zhengzhou area, the monitoring site will be affected by the transport of industrial emission NMVOCs.

   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.

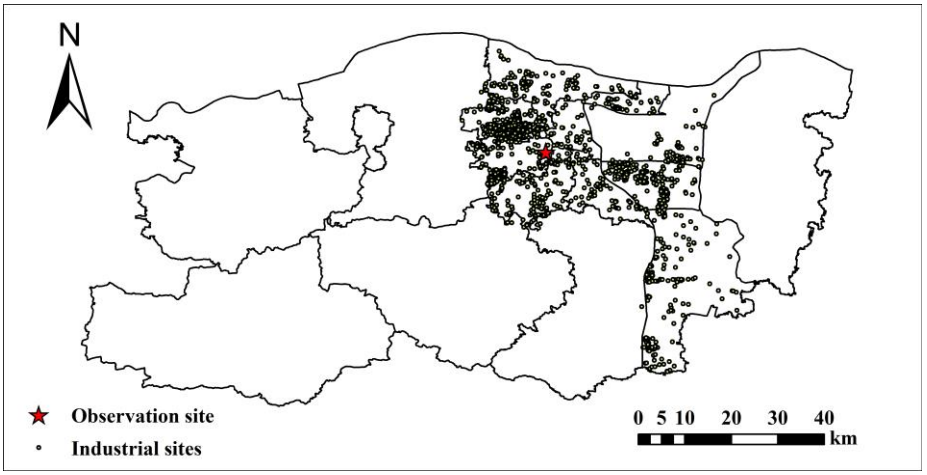

Fig. 1 Distribution of industrial sites around observation sites.

3. We have performed the PMF analysis on both clean days and polluted days simultaneously. Fig. 2. shows the source profiles and contributions of NMVOCs in Case 1. From Figure 3, we can see that the contributions of combustion, industrial production, biogenic emission, vehicular exhaust, LPG/NG, and solvent usage are 8.9, 23.9, 4.4, 29.7, 7.3, and 25.7%, respectively. Compared with the Case 1 event in the manuscript, the differences in contributions of each factor are not significant. Vehicular exhaust, solvent usage, and biogenic emission decrease by 0.3, 1.3, and 1.2% respectively, while combustion, industrial production, and LPG/NG increase by 0.9, 0.9, and 0.3% respectively. Fig. 4. shows the source profiles and contributions of NMVOCs in Case 2. From Figure 5, we can see that the contributions of combustion, industrial production, biogenic emission, vehicular exhaust, LPG/NG, and solvent usage are 10.7, 20.0, 7.2, 16.6, 19.5, and 26.1%, respectively. Compared with the Case 2

event in the manuscript, industrial, biogenic emission, LPG/NG, and solvent usage decrease by 1.0, 0.8, 1.5, and 1.9% respectively, while combustion, biogenic emission, and vehicular exhaust increase by 3.7% and 2.6%. Fig. 6. shows the source profiles and contributions of NMVOCs in clean days. From Figure 7, we can see that the contributions of combustion, industrial production, biogenic emission, vehicular exhaust, LPG/NG, and solvent usage are 11.4, 19.6, 3.6, 33.6, 5.4, and 26.4%, respectively. Compared with the clean days in the manuscript, industrial and vehicular exhaust decrease by 1.5% and 1.4%, while combustion, biogenic emission, LPG/NG, and solvent usage increase by 0.4, 0.6, 0.4, and 1.4%, respectively. From the above analysis, it can be seen that although performing PMF separately on clean days and polluted days may lead to some differences, the relative contributions of each factor in Case 1, Case 2, and clean days have not changed. Compared to the manuscript, the main conclusions remain consistent, namely that vehicular exhaust, solvent usage, and industrial production were major contributors to both O_3 pollution events and clean days.

4. We appreciate the emphasis on the importance of Secondary NMVOCs, such as OVOCs and amines, in identifying NMVOCs sources. According to your request, we reperformed PMF to attempt to analyze the contribution of secondary formation to NMVOCs. However, we

found that the secondary formation source obtained always contain trace substances from other sources, and these substances contribute significantly. Additionally, we reviewed the literature and found that these trace substances from other sources are also present in the secondary formation source in the literature (Zhang et al., 2023;Wen et al., 2024;Zeng et al., 2023), but the authors did not explain this phenomenon. We believe that there may be a significant error in the secondary formation source obtained through PMF analysis in this study. Therefore, we did not further analyze the contribution of secondary formation source to NMVOCs in this study. Once again, we appreciate your suggestions and guidance. In future studies, we will carefully and thoroughly analyze the secondary formation source of NMVOCs.

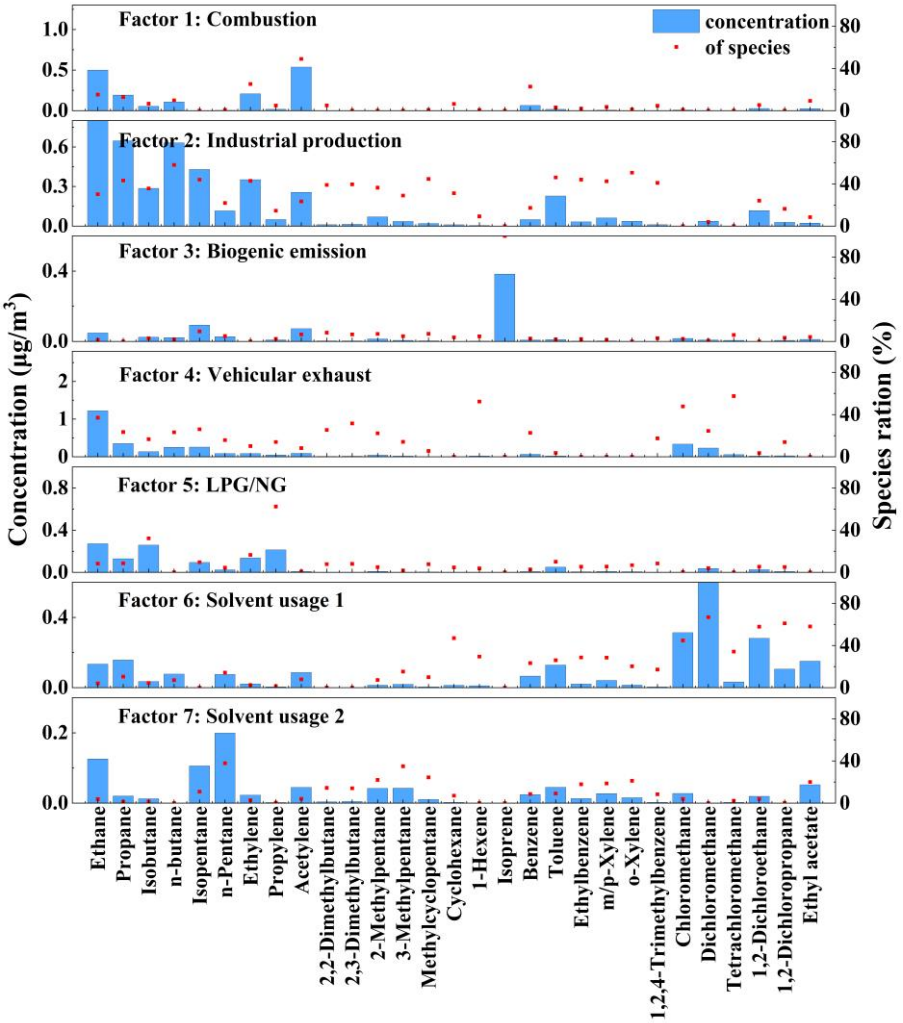

Fig. 2. Source profiles and contributions of NMVOCs in Case 1.

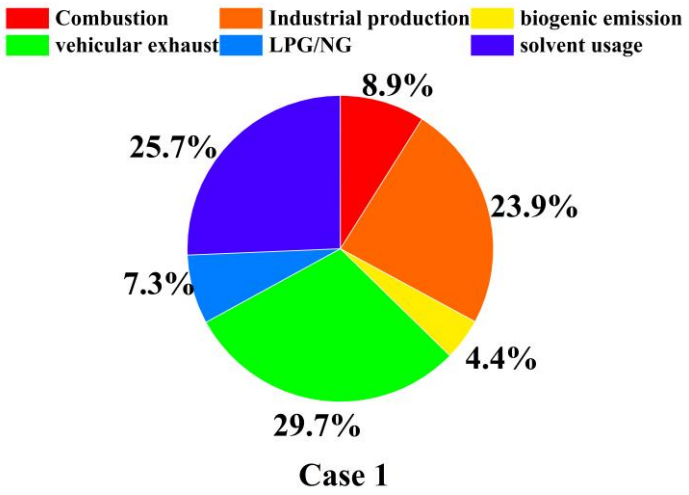

Fig. 3. Source contributions to NMVOCs concentration in Case 1.

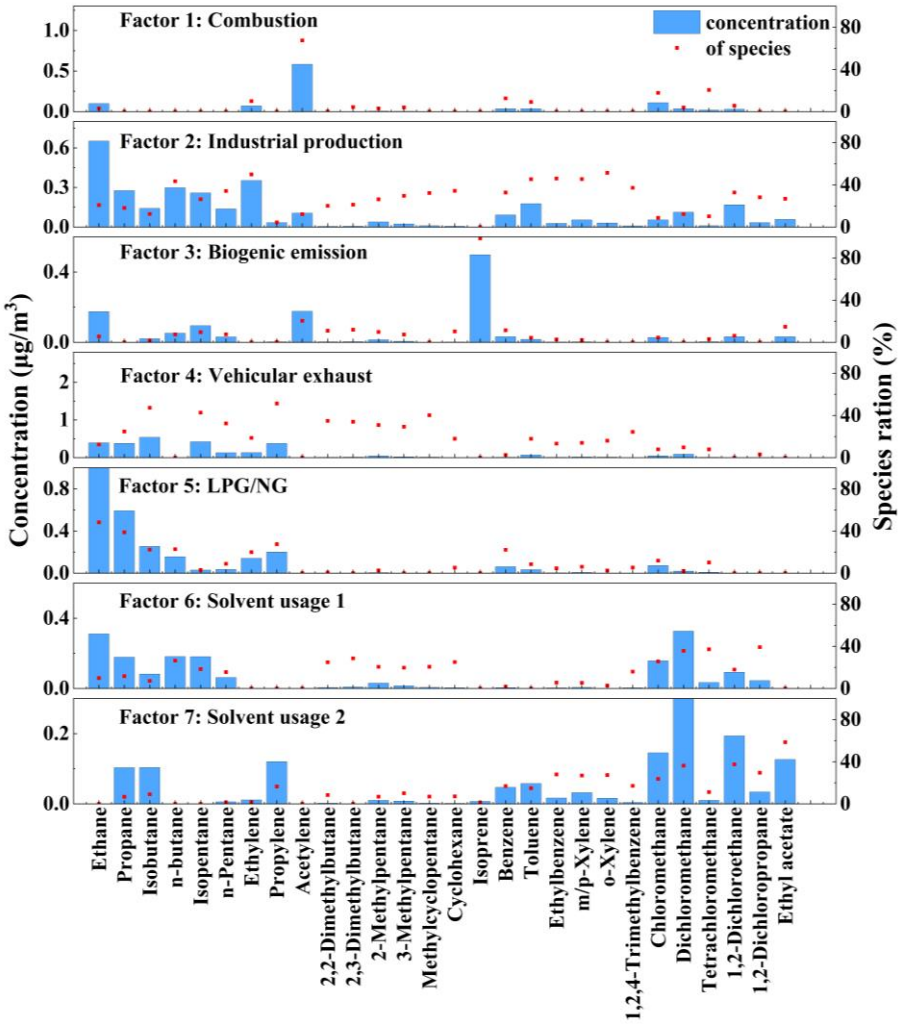

Fig. 4. Source profiles and contributions of NMVOCs s in Case 2.

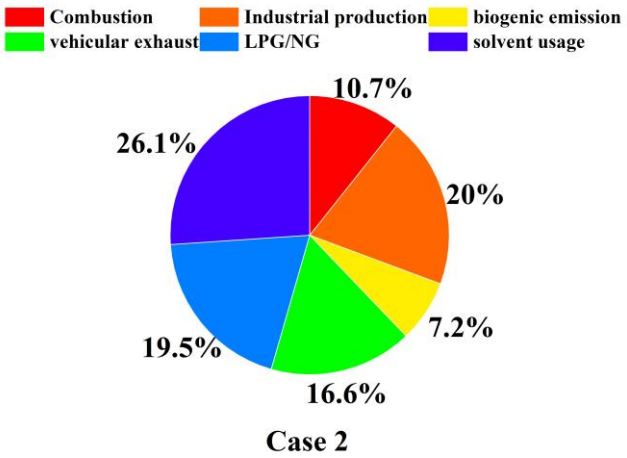

Fig. 5. Source contributions to NMVOCs concentration in Case 2.

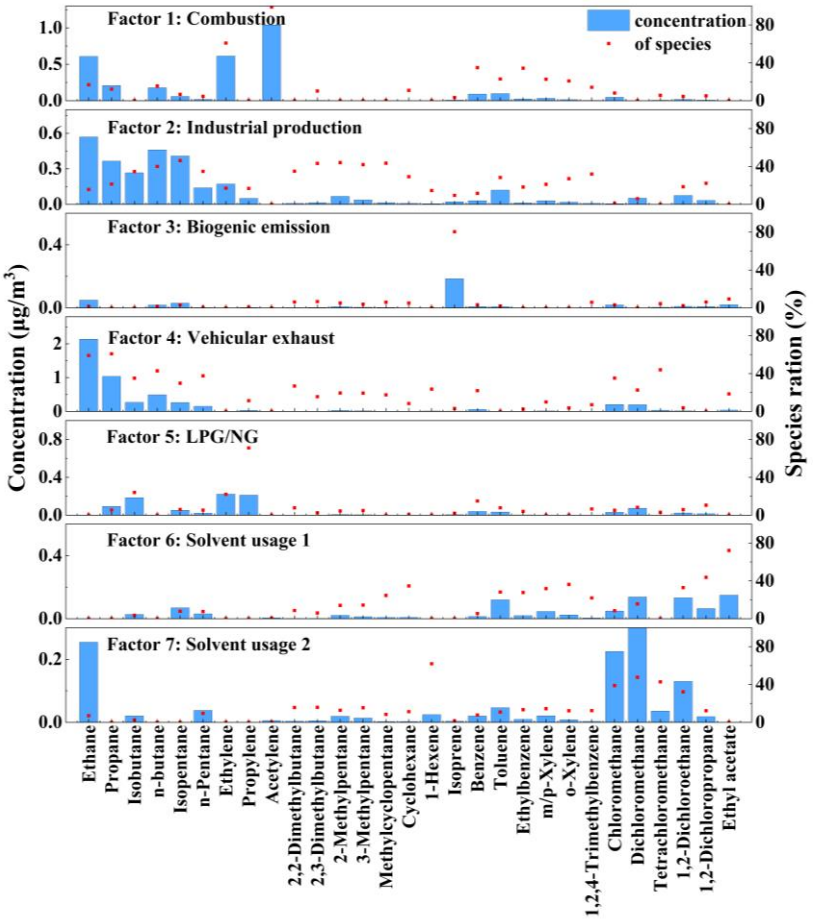

Fig. 6. Source profiles and contributions of NMVOCs s in Case 2.

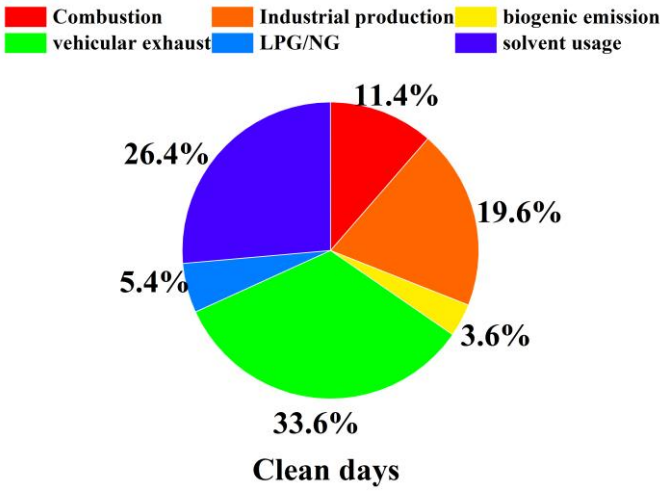

Fig. 7. Source contributions to NMVOCs concentration in Case 2.

More explanation is required for Figure 5.

Liness 366-369 indicate that similar sources contribute to O_3 pollution events and clean days. Does it mean that the emissions of primary

and secondary VOCs do not influence O_3 formation? Then, what are the reasons for O_3 formation in the area?

Response: Thank you for your comments.

1. In this study, the contributions of various pollution sources show relatively minor differences between O_3 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 O_3 pollution.
2. Although compared with the pollution process, the contribution changes of each pollution source in O_3 pollution events are not very obvious. It does not mean that the emissions of primary and secondary NMVOCs do not influence O_3 formation. In fact, emissions of both primary and secondary NMVOCs are important factors in O_3 formation. The reasons for O_3 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.
3. We compared the average concentrations of nitrogen oxides in Case 1,

Case 2, and clean days. The average concentrations of NO_2 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 NO_2 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 NO_2 can promote the formation of O_3, while the titration reaction between NO and O_3 consumes O_3. 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.

4. We further explored the relationship between meteorology and O_3 concentration. According to Fig. S3a and Fig. S3b, it can be observed that O_3 concentration shows a linear increasing trend with temperature and a linear decreasing trend with RH. O_3 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 O_3 pollution. Fig. S3c indicates that O_3 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 O_3 concentration consistently exceeds the

secondary standard. Wang et al. argued that most of the reactions involved in ozone formation increase with temperature, and the rate of ozone production exceeds that of ozone loss by a large margin (Meng et al., 2023).

In conclusion, in addition to the impact of solvent usage, biogenic emission, and LPG/Ng on O_3 pollution events, meteorological factors are also significant factors in the occurrence of O_3 pollution events.

In addition, we have added an analysis of the correlation between O_3 and temperature and RH in the manuscript. (Line 235-253)

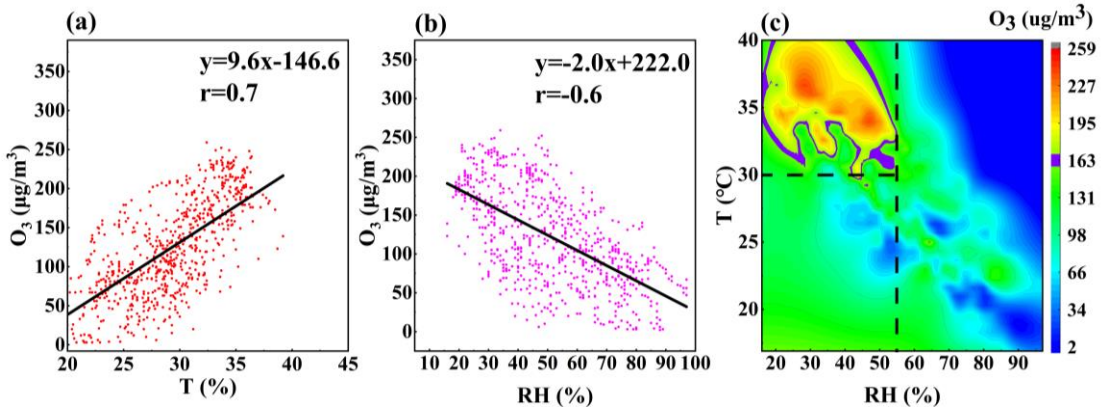

Fig. S3 Correlation analysis of O_3, T, and RH.

Line 235-253: The average concentrations of TNMVOCs, NO_2, PM_{10}, and $PM_{2.5}$ on clean days were lower than those of the O_3 pollution events. The average RH (65 ± 17%) on clean days was higher than those during Case 1 and Case 2 events, while the average temperature (26.0 ± 4.8 °C) was lower than those during Case 1 and Case 2 events. According to the analysis in Fig. S3a and Fig. S3b, O_3 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 O_3 pollution. Fig. S3c indicates that O_3 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 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.

Section 3.3.1 O_3 **sensitivity analysis**

Line 383 indicates that O_3 formation is more sensitive to biogenic emissions. Why is that? Add references to previous studies in urban settings, how AVOCs and BVOCs vary and their effect on ozone levels.

Response: Thank you for this valuable comment.

In summer, due to higher solar radiation, biogenic emissions are an important source of NMVOCs. Studies in Yucheng (Zong et al., 2018), Leshan (Xie et al., 2021), and and Nanjing (Fan et al., 2021;Ming et al., 2020) have shown that ozone 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 ozone exhibits greater sensitivity to BVOCs than AVOCS during hot seasons. Wang et al. (2019) found in their study on O_3 source apportionment in Henan Province, where Zhengzhou is located, that BVOCs contribute to approximately 23.9% of the O_3 attributed to NMVOCs. Previous studies on O_3 sensitivity analysis in Zhengzhou have shown a strong sensitivity of O_3 to BVOCs. Wang et al. pointed out that in two O_3 pollution events that occurred, O_3 exhibited higher sensitivity to BVOCs than AVOCs.

Furthermore, research in other regions has also indicated a higher sensitivity of summer O_3 to BVOCs. The time of this study is in the summer months with the highest temperature, which is more conducive to plant emissions.

In response to your query regarding the reasons for this sensitivity, we have incorporated references to previous studies conducted in urban settings that have discussed the variations of AVOCs and BVOCs and their impact on ozone levels. By including this additional information and discussing the relevant literature, we aim to have provided a more comprehensive analysis of the factors influencing O_3 formation. More analysis has been provided in the revised manuscript to clarify this aspect more effectively. (Line 449-459)

Line 449-459: 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 O_3 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 O_3 formation potential. Studies in Yucheng (Zong et al., 2018), Leshan (Xie et al.,

2021), and and Nanjing (Fan et al., 2021;Ming et al., 2020) have shown that O_3 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 O_3 exhibits greater sensitivity to BVOCs than AVOCS during hot seasons. Wang et al. (2019) found in their study on O_3 source apportionment in Henan Province, where Zhengzhou is located, that BVOCs contribute to approximately 23.9% of the O_3 attributed to NMVOCs. Therefore, the contribution of biogenic NMVOCs to O_3 is very important.

Line 382-383 What could be the possible reasons for the RIR of BVOCs being higher than AVOCs? What are the biogenic VOCs species you have included in this analysis? Add these details in the section.

Response: Thank you for this valuable suggestion.

The average RIR value for BVOCs was higher than that for AVOCs, primarily due to the elevated BVOCs emissions under conditions of higher temperature and solar radiation, along with their high reactivities and ozone formation potential. Our study focused on the period when summer temperatures and solar radiation are at their highest, resulting in peak biogenic emissions of BVOCs. Furthermore, the monitoring sites were surrounded by abundant vegetation cover. Isoprene was the sole BVOCs considered in this analysis. Isoprene is an important tracer to indicate biogenic

emissions. Currently, many studies use Isoprene to represent BVOCs (Xie et al., 2021;Li et al., 2024;Qin et al., 2023). We have incorporated these details in manuscript. (Line 449-459)

Figure 6: The RIR (%) looks similar for every case. Even for clean days, aromatics show higher values than polluted events. I suggest to check the values.

Another section should be added to compare the study results with the source apportionment studies in the city in different periods or seasons. Also, comparison with other Chinese cities studies can add extra value to the analysis.

Response: Thank you for the valuable feedback and suggestions. We have carefully checked the original data and confirmed that there are no issues with the results. The RIR values for different species/groups are shown in Table 1. The RIR value for aromatics on clean days is indeed greater than the RIR value for O_3 pollution events, indicating that the generation of O_3 is more sensitive to alkenes on polluted days, while on clean days, the generation of O_3 is more sensitive to aromatics.

Table 1. Average RIR values of the O_3 for different species/groups during different processes in Zhengzhou.

	AVOCs	BVOCs	CO	NO_x	Alkanes	Alkenes	Aromatics
Entire period	3.44	4.48	0.74	-7.9	0.67	1.13	1.17
O_3 pollution events	3.44	5.3	0.66	-8.4	0.69	1.2	1.09

Clean days	3.88	4.57	0.93	-6.9	0.65	1.17	1.47

We are a little confused about the suggestion to add a comparison of source apportionment results, because Figure 6 does not cover source apportionment. Source apportionment is in Section 3.2.2, so we have followed your suggestion to add some content in Section 3.2.2 to compare the results of this study with source apportionment studies of different periods or seasons in the city. In addition, we have also considered comparing the study results with studies in other Chinese cities to add value to the analysis. (Line 414-434)

Line 414-434: In summary, the observation sites are significantly influenced by vehicular exhaust, solvent usage, and industrial production. The results of this study show similarities in the source apportionment of NMVOCs in Zhengzhou during the summers of 2018 to 2021 (Yu et al., 2022;Guo et al., 2024). Yu et al. (2022) found that vehicular exhaust and industrial production contributed the most to NMVOCs emissions in Zhengzhou from 2018 to 2020, with the main sources of summer NMVOCs being vehicular exhaust, solvent usage, and industrial production. In contrast to the NMVOCs source apportionment results of Li et al. (2021). for the O_3 pollution process in Zhengzhou in May 2018, the difference lies in the higher impact of solvent usage compared to vehicular exhaust

and industrial production. This is mainly attributed to the fact that Li et al. (2021)'s observation site was located within Zhengzhou University, making them more susceptible to the influence of chemical reagent use. In comparison to the source apportionment of NMVOCs in Zhengzhou during winter (Zhang et al., 2021), combustion also becomes an important contributor during winter, attributed to the increased heating demand, while the contribution from solvent usage is relatively lower due to the cold temperatures. In comparison with other cities (Table S2), vehicular exhaust in Zhengzhou contributes the most, higher than in cities such as Qingdao (Wu et al., 2023), Xuchang (Qin et al., 2021)), Guangzhou (Meng et al., 2022), Nanjing (Fan et al., 2021), Shijiazhuang (Guan et al., 2020), and Weinan (Hui et al., 2020), but lower than in Changzhou (Liu et al., 2023) and on par with Beijing (Liu et al., 2020). Solvent usage in Zhengzhou contributes more than in Qingdao (Wu et al., 2023), Xuchang (Qin et al., 2021), Nanjing (Fan et al., 2021), Shijiazhuang (Guan et al., 2020), Weinan (Hui et al., 2020), Changzhou (Liu et al., 2023), and Beijing (Liu et al., 2020), but less than in Guangzhou (Meng et al., 2022). Industrial production in Zhengzhou contributes more than in Xuchang (Qin et al., 2021), Guangzhou (Meng et al., 2022), Nanjing (Fan et al.,

2021), Weinan (Hui et al., 2020), and Changzhou (Liu et al., 2023), but less than in Shijiazhuang (Guan et al., 2020).

Section 4 Conclusions:

The authors have just given a summary of the results obtained. No explanation is included about why and how any trend follows the study of how sources influence O_3 formation in the area. What could be the driving factors for the presence of any particular source? You should include more details in the section.

Response: Thank you for the valuable suggestion regarding our study.

We have revised the conclusion section in the revised manuscript to integrate all results, rather than just summarizing the key findings of each section in turn. We strive to better demonstrate the overall significance and contribution of the research. Thank you once again for your feedback, and we have taken it into consideration and made the necessary changes. (Line 532-551)

Line 532-551: The summer O_3 pollution has always been an important environmental issue in Zhengzhou. This study investigated the characteristics and emission sources of O_3 precursors from 1st to 30th June 2023. The OBM was used to analyze the influence of precursors on the formation of O_3, and the

emission reduction strategy of precursors was proposed to control the concentration of O_3. 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 O_3 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 NO_2 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 O_3 precursors is one of the reasons for the formation of O_3 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 O_3 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 VOCs. The increase of solvent usage, biogenic emission and LPN/NG contribution is an important cause of O_3 pollution. Sensitivity analysis of O_3 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 O_3 formations were in the AVOCs-limited regimes, which means reducing the concentration of AVOCs was an effective way to reduce O_3 concentration. Meanwhile, we suggest that the minimum reduction ratio of AVOCs/NO_x should be no less than 3:1 to reduce O_3 production.

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