Reviewer #1:

We do appreciate your constructive and useful comments. To better reply to your general comments in your long paragraph, we have divided your comments into serval parts with superscript [a, b, c], etc., and correspondingly addressed your comments in a separate paragraph [a, b], etc. More detailed replies for the same topic are shown in your specific comments. To facilitate your review, the comments are in black, and the responses are in blue.

Detailed comments:

The article explored the relationship between VOCs and $PM_{2.5}$ with abundant VOCs species observed in Zhengzhou during the COVID-19 and made recommendations for the control of VOCs source emissions. [a]The current discussion may not be sufficiently supportive, please add more details to each section to make the entire article more logical.

[b]Basic details regarding instrumentation and data collection are missing. The authors need to supplement materials related to the reliability of the PMF results.

[c]Further more, more work is needed to elucidate the relationship between VOCs and haze pollution, as well as the influencing factors. And it is

suggested that model simulation on SOA formation potential be added to the manuscript.

While the theme and results of the study are interesting, I have provided a few suggestions for improvement.

Response: We are very grateful for the positive comments and suggestions. We have separately replied your suggestions into three parts as following:

[a]The current discussion may not be sufficiently supportive, please add more details to each section to make the entire article more logical.

We will overhaul every section of the revised version. In each chapter we will add more discussion to make the entire article more logical and comprehensive. Details can be found in the following point-to-point response.

[b]Basic details regarding instrumentation and data collection are missing. The authors need to supplement materials related to the reliability of the PMF results.

Additional details about the instruments and data collection are provided below.

For instrumentation comments, please see our replies in the following

specific comments.

Reliability of PMF results will be added to the text with relevant figures and tables in the supplementary materials.

We used displacement of factor elements (DISP) to assess PMF modelling uncertainty (for a description, see Paatero et al. (2014)). Q was less than 1% and no swaps occurred for the small est dQmax in DISP. Fpeak values from -2 to 2 were tested to explore the rotational stability of the solutions. Q_{true}/Q_{exp} is lowest when Fpeak = 0, so we chose the PMF results for that case.

After examining 3-8 factors, 20 base runs with 5 factors eventually selected to represent the final result. We provide an explanation of factor selection in the supplementary materials. Figure 3(a) includes Q_{true}/Q_{exp}, Q_{robust}/Q_{exp} for factors 3-8. The slopes of these two ratios in changed at five factors, and we found that five factors were more realistic after repeated comparisons of the results at four, five and six factors. These five factors eventually selected as potential sources for the observed VOCs are: (1) Fuel evaporation; (2) Solvent usage; (3) Vehicular emission; (4) Industrial source; and (5) Combustion.

References:

Paatero, P., Eberly, S., Brown, S. G., Norris, G. A.: Methods for

estimating uncertainty in factor analytic solutions, Atmospheric Measurement Techniques, Volume 7, 781-797, https:// 10.5194/amt-7-781-2014, 2014.

[c]Further more, more work is needed to elucidate the relationship between VOCs and haze pollution, as well as the influencing factors. And it is suggested that model simulation on SOA formation potential be added to the manuscript.

It is well known that VOCs are precursors for ozone formation and generation of secondary organic aerosols (SOAs). The O_3 pollution per se is not really a haze event. However, O_3 can assist the formation of fine particulates; there are numerous studies about the so-called double pollution of O_3 and $PM_{2.5}$. O_3 as an oxidant can improve the oxidation capacity and promote the oxidation of SO_2 and NO_2 (Li et al., 2023). On the other hand, the suppression of O_3 formation due to the presence of $PM_{2.5}$ has recently been highlighted for further O_3 pollution controls in regions that suffer high ozone concentrations (Zhang et al., 2024). Furthermore, $PM_{2.5}$ decreased the surface photolysis rates J_{NO2} and J_{O1D}, resulting in a decrease in O_3 concentration in the VOC-sensitive area and a slight increase in the NO_x-sensitive area (Qu et al., 2023.). SOAs themselves are of course part of organic aerosols in $PM_{2.5}$ haze conditions.

The factors affecting VOC-haze interactions are typically atmospheric photochemistry and the mixing ratio of NOx and type of VOCs in generating SOAs. However, most *VOC species posed no non-carcinogenic risk during haze events (Zhang et al., 2021).*

Additionally, we have included quantitative analysis for SOA as well. In particular, Figure 1 shows the SOAP concentrations and contribution rates of the top ten species throughout the entire process, during two pollution processes, and clean days. The top ten species all reached close to 100% of the total SOAP contribution, with Case 1 reaching 98%. The composition of the top ten species is basically the same for each process. Toluene, m/p-xylene, and benzene were consistently the top three species. Toluene, the highest contributing species, reached a SOAP value of 49.4 $\mu g/m^3$ in the most polluted Case 2, which was 3.2 times higher than the SOAP sum of all species on the clean day (15.5 $\mu g/m^3$). The SOAP value for Case 1, which is also a contaminated process, was 67 $\mu g/m^3$, and the main species including toluene (34.6 $\mu g/m^3$) were lower than those for Case 2 (m/xylene: 9.8 $\mu g/m^3$, benzene: 8.5 $\mu g/m^3$) (m/xylene: 19.4 $\mu g/m^3$, benzene: 13.4 $\mu g/m^3$).

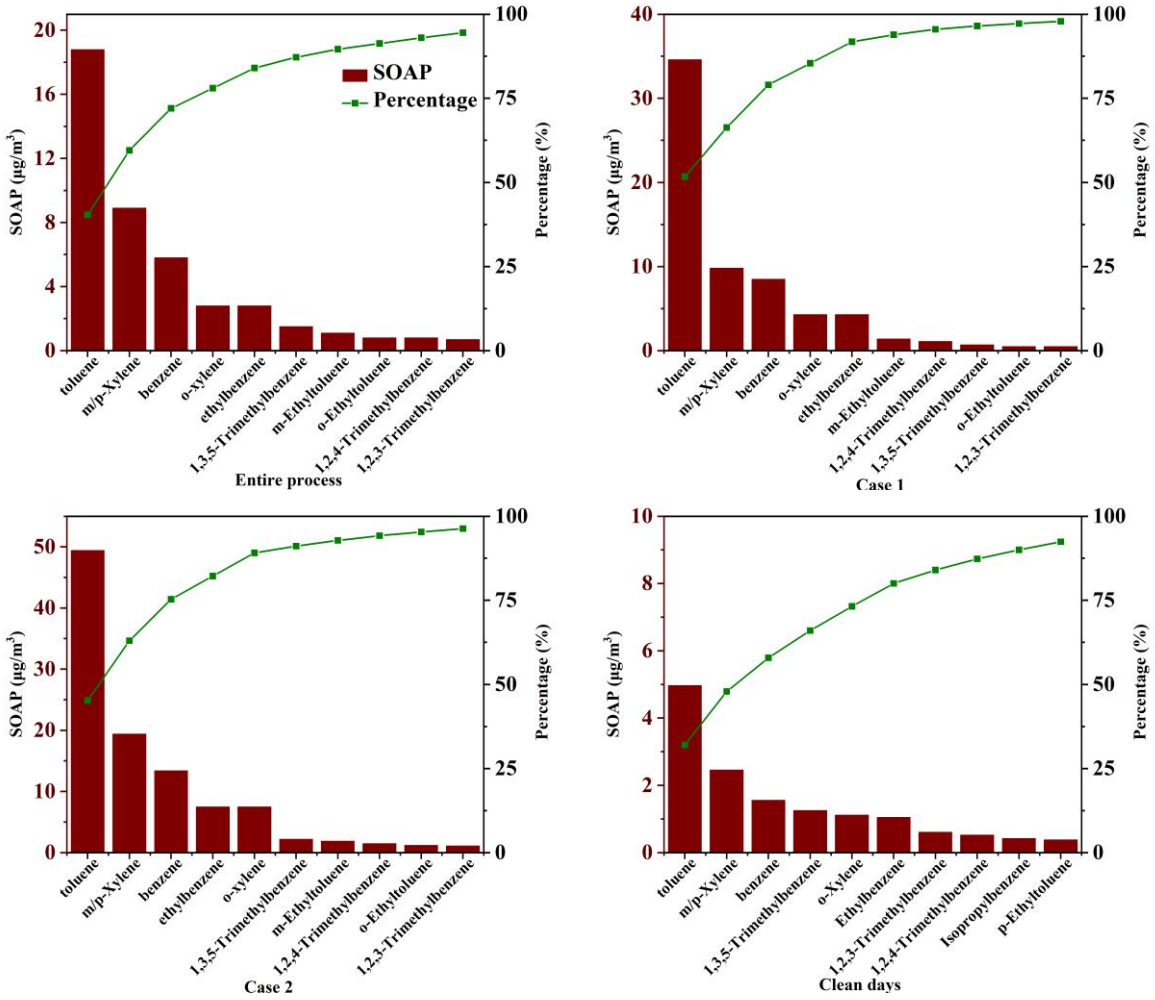


Figure 1. SOAP dominant species in different processes

The following is point-by-point responses to all your comments and valuable suggestions.

References:

Qu, Y.: The underlying mechanisms of $PM_{2.5}$ and O_3 synergistic pollution in East China: Photochemical and heterogeneous interactions, Science of The Total Environment, Volume 873, https://doi.org/10.1016/j.scitotenv.2023.162434, 2023.

Li, Y.: Spatiotemporal Variations of PM2.5 and O3 Relationship during 2014–2021 in Eastern China, Aerosol and Air Quality Research, https://doi.org/10.4209/aaqr.230060, 2023.

Zhang, D.: Characteristics, sources and health risks assessment of VOCs in Zhengzhou, China during haze pollution season, Journal of Environmental Sciences, Volume 108, https://doi.org/10.1016/j.jes.2021.01.035, 2021.

Zhang, J.: Enhanced summertime $PM_{2.5}$-suppression of O_3 formation over the Eastern U.S. following the O_3-sensitivity variations, Environmental Science: Atmospheres, 2024.

1. Line 124-135: The authors lack more detailed descriptions of the instrumentation. What are the working procedures of the instruments? What is the time resolution of the samples? How long were the samples collected for? Where were they captured? It is recommended to include information about instrument quality control methods.

Response: As per your comments, we have added a description of instrumental details including time resolution to the Materials and Methods section:

The VOCs were measured hourly using a GC-FID/MS (*TH-PKU 300 b*, Wuhan Tianhong Instruments Co., China). The instrument TH-PKU300b

includes electronic refrigeration ultra-low temperature pre-concentration sampling system, analysis system and system control software. The ambient VOCs in the first 5 minutes of each hour were collected by the sampling system and then entered the concentration system. Under low temperature conditions, the VOCs samples collected were frozen in the capillary capture column, and then quickly heated and resolved, so that the compounds entered the analysis system. After separation by chromatographic column, the compounds were monitored by FID and MS detectors. During the detection process, the atmospheric samples collected undergo analysis through two distinct pathways. C2-C5 hydrocarbons are analyzed using FID, while C5-C12 hydrocarbons, halocarbons, and OVOCs are analyzed with a MS detector. After excluding species with missing data exceeding 10%, the detected volatile organic compounds include 29 alkanes, 11 alkenes, 17 aromatics, 35halocarbons, 12 OVOCs, 1 alkyne (acetylene), and 1 sulfide (CS_2) with a total of 106 compounds.

As for information on instrument quality control methods, the revised text shall be:

The instrument was calibrated per week to ensure the accuracy of VOCs by injecting standard gases with a five-point calibration curve. The detection limit of C2-C5 hydrocarbons ranges from 0.007 to 0.099 ppbv,

other hydrocarbons are 0.004–0.045 ppbv, halogenated hydrocarbons 0.009-0.099 ppbv, OVOCs and other compounds of 0.006–0.095 ppbv. Thirty-two of the monitored VOCs had more than 90% of their data greater than the detection limit, and 34 had more than 50% of their data greater than the detection limit.

2. Section 2.2 Positive Matrix Factorization (PMF) model

How did the authors conduct factor selection, and why did not choose the 5-factor solution, 6-factor solution, and 7-factor solution? The authors need to provide more explanations and justifications in the manuscript.

Response: After examining 3-6 factors, 20 base runs with 5 factors eventually selected to represent the final result. We provide an explanation of factor selection in the Supplementary Materials. Figure 2(a) includes Q_{true}/Q_{exp}, Q_{robust}/Q_{exp} for factors 3-8. The slopes of these two ratios in changed at five factors, and we found that five factors were more realistic after repeated comparisons of the results at four, five and six factors. These five factors eventually selected as potential sources for the observed VOCs are: (1) Fuel evaporation; (2) Solvent usage; (3) Vehicular emission; (4) Industrial source; and (5) Combustion. Five factors have been commonly reported before, e.g., in Shijiazhuang, northern China (Guan et al, 2023) and in Beijing (Cui et al., 2022). Figure 2(b) shows the result of Fpeak model run; Q_{true}/Q_{exp} is lowest when Fpeak

= 0, so we chose the PMF results for that case.

The above statement will be incorporated into the revised text.

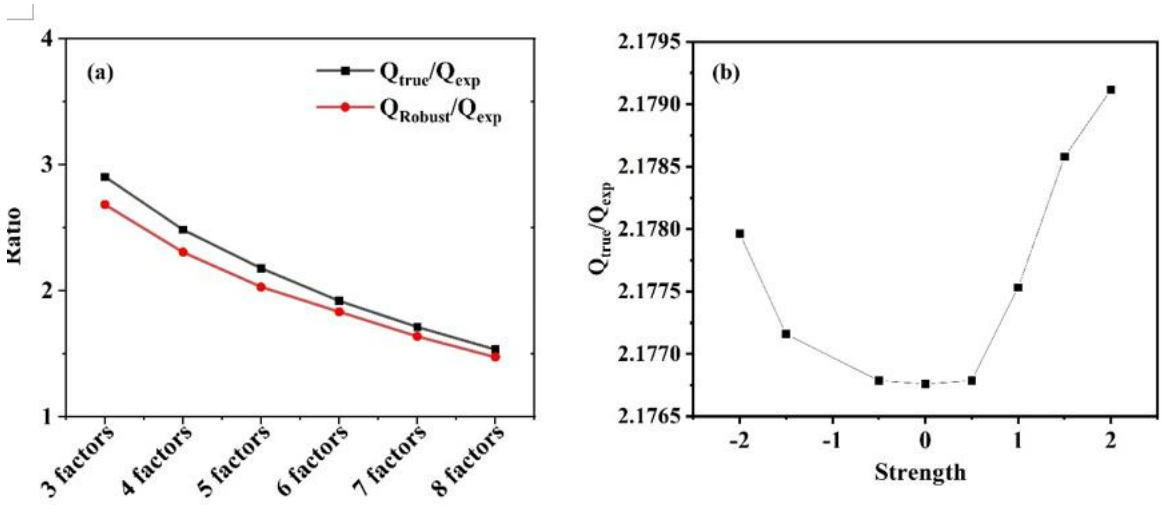


Figure 2. (a) The $Q_{true}/Q_{expected}$ ratios in different solutions; (b) the $Q_{true}/Q_{expected}$ ratio for different Fpeak value solutions.

References:

Cui, L., Wu, D., Wang, S., Xu, Q., Hu, R., and Hao, J.: Measurement report: Ambient volatile organic compound (VOC) pollution in urban Beijing: characteristics, sources, and implications for pollution control, Atmospheric Chemistry and Physics, 22, 11931-11944, https://doi.org/10.5194/acp-22-11931-2022, 2022.

Guan, Y., Liu, X., Zheng, Z., Dai, Y., Du, G., Han, J., Hou, L. a., and Duan, E.: Summer O3 pollution cycle characteristics and VOCs sources in a central city of Beijing-Tianjin-Hebei area, China,

Environmental Pollution, 323, 121293, https://doi.org/10.1016/j.envpol.2023.121293, 2023.

3. Section 3.1 Pollution characteristics

Line 194: Ensure that the font in the figures is consistently in Times New Roman. The y-axis labels do not match the legend (NO and NO_x).

Response: We have revised the manuscript according to your comments.

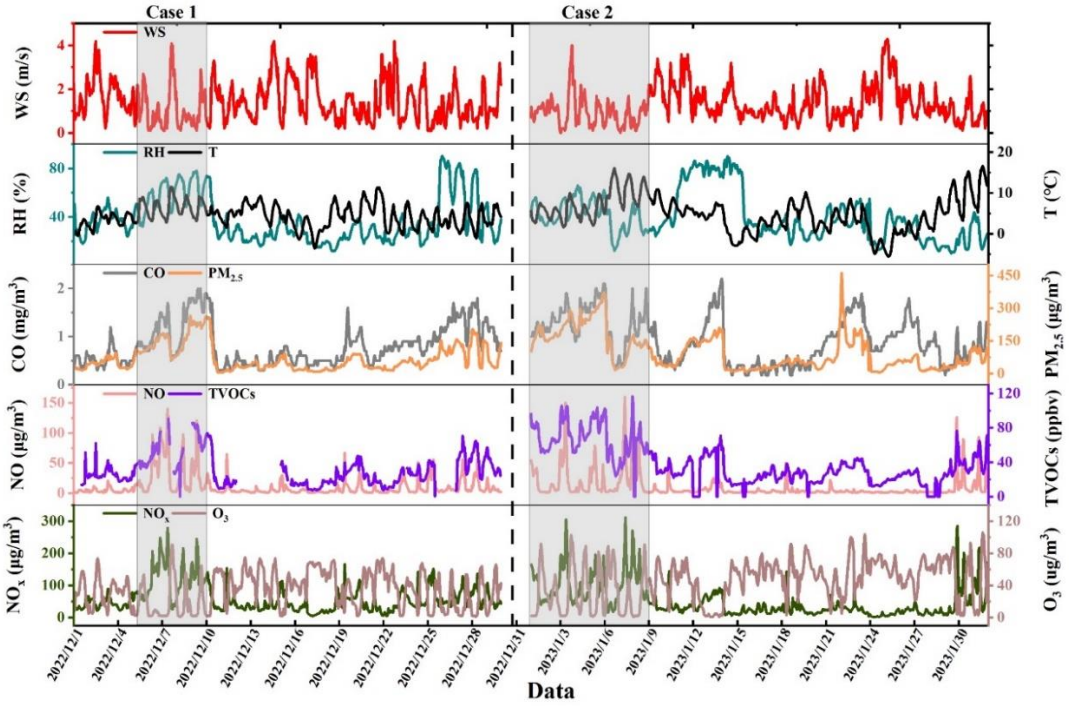


Figure 3. Time series of WS, WD, T, RH, CO, $PM_{2.5}$, NO, TVOCs, NO_x and O_3 during the observation period.

4. What does the shading in Figure 1 represent? What are Case 1, Case 2,

Case 3, Case 4, and Case 5? Clear explanations need to be provided. If these cases represent haze pollution processes, how do you define your pollution processes? Please include the references you consulted.

Response: The shadow section in Figure 3 represents two haze pollution events during the monitoring period. A pollution event is determined when the daily average concentration of $PM_{2.5}$ exceeds 75 μg/m^3 (China's II-level standard) for at least three consecutive days. We apologize for the unclear statement and recognize that the original annotations might confuse readers, so we simplify the labeling in Figure 1. To avoid misinterpretation, we deleted processes with no more than 3 days of continuous contamination in Figure 3. In the revised version, we focus on the distinct characteristics of Case 1, Case 2, and Clean days as depicted in the figure. Case 1 (December 5 to December 10 with daily average $PM_{2.5}$ = 142.5 μg/m^3) and Case 2 (January 1 to January 8 with daily average $PM_{2.5}$ = 181.5 μg/m^3) were selected as they represent the pollution events in infection and recovery periods, respectively, due to their long duration and high pollution levels. We divided this period into an infection period (1-30 December 2022) and a recovery period (1 January 2023-31 January 2023) based on Chinese Center for Disease Control and Prevention's December 2022-January 2023 infection data statistics (Figure 4). Any days with a $PM_{2.5}$ concentration lower than 35 μg/m^3 (China's I-level standard) is considered as Clean days.

The above definition of pollution process will be incorporated into the revised manuscript.

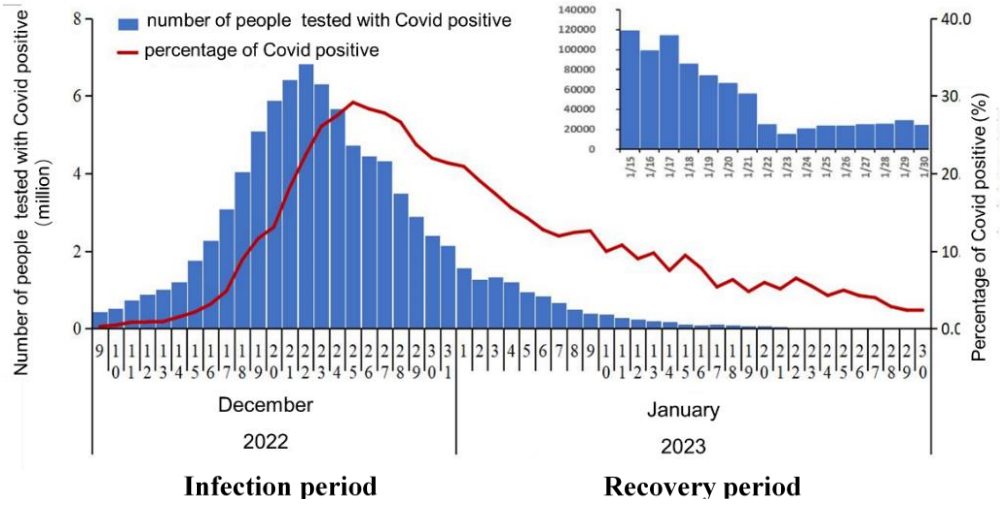


Figure 4. Trend of Omicron infection in China from 9 Dec. 2022 to 1 Jan. 2023 (CCDCP, 2023)

5. Line 217-225: Why did you only discuss Case 1 and Case 3? Are these two periods particularly significant? Provide your reasoning.

Response**:** In this study, a continuous online observation of VOCs was carried out, which covered the abolishment of lockdown measures in Zhengzhou. A two-month-long lockdown measure was applied after first Omicron case of student in Zhengzhou University was confirmed on October 8, 2022. Lockdown measure was abolished from the beginning of December in 2022, which resulted in a sharp increase of Omicron-infected people and a decrease in daily social production activities. In fact, the "Nucleic Acid Screening Measures for all staff" policy was also

canceled on December 8 in 2022. People are basically homebound after the lifting of the lockdown policy due to either infection or fear of infection of Omicron variant. Due to herd immunization, people resumed normal life and industry normal activity. Therefore, the characteristics and variations of VOCs during different periods were investigated to assess their impact on pollution in general and on the formation of SOA in particular and to provide data support for future pollution control policies in Zhengzhou.

During the pollution events that occurred in the observation phase, Case 1 (December 5 to December 10) and Case 2 (January 1 to January 8) were considered to be in the early stages of infection and recovery periods, respectively. These two cases have long durations and high pollution levels, making them representative pollution processes for the infection and recovery periods. To avoid misinterpretation, we deleted processes with no more than 3 days of continuous contamination in Figure 1. Essentially, Case 3 in the original paper now is Case 2.

6. In Figure 2, the font should be changed to Times New Roman.

Response: We have modified in the revised manuscript according to your suggestions for the consistent font.

7. In this section, you only analyzed the variations in pollutant

concentrations and meteorological conditions. What is the relationship between them? Which factors are crucial causes of pollution? You have not provided analysis and explanations.

Response: The pollutant emission from different sources is the main cause of pollution. Indeed, meteorological conditions play an important role in the extent of pollution. But we know that the changes in emissions from pollution sources over a period of time are usually small, and meteorological conditions play a very important role in the formation of pollution. And previous studies have also shown that low wind speed, high relative humidity, and low precipitation are meteorological factors that contribute to the worsening of particulate matter pollution in Zhengzhou during winter (Duan et al., 2019). The meteorological conditions in the two periods are generally similar, and the Case 2 in the recovery periods are slightly more prone to atmospheric stability, high relative humidity and other meteorological conditions that are not conducive to the dispersion of pollutants than Case 1 in the infection periods. However, this slight meteorological difference cannot directly lead to a significant change in the degree of pollution we have observed. Clearly, the extent of pollution in different periods is mainly due to anthropogenic activities and to a lesser extent, regional transport (see the following reply), and not meteorological conditions. The reason for providing meteorological data is to add supplementary information for

these events.

Based on your comments, we have studied the relationship between meteorological conditions and the concentration of different pollutants. We found a significant correlation between relative humidity and the following three pollutants (Figure 5). It shows that changes in relative humidity have an important effect on pollution formation.

We will supplement this part according to your comments as: We analyzed the relationship between meteorological parameters and pollutant concentrations and found correlations between $PM_{2.5}$, TVOCs and NO_x and RH, suggesting that meteorological conditions have an important influence on pollution formation.

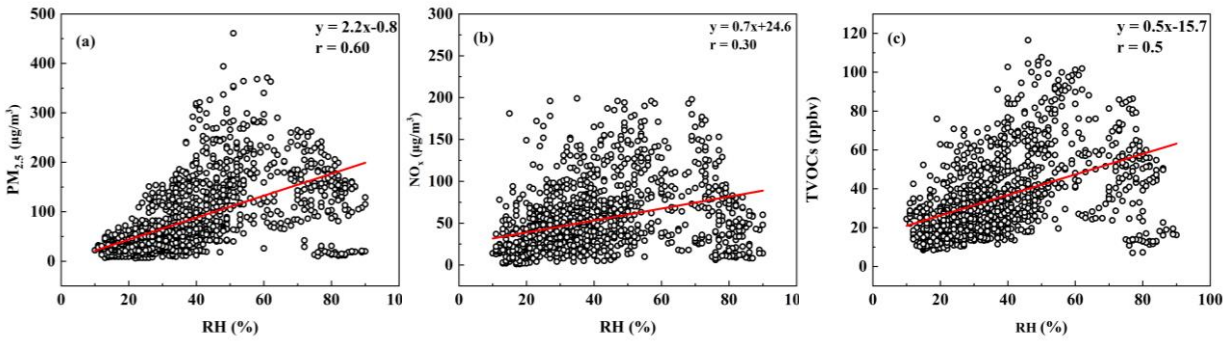


Figure 5. Relative humidity and (a) $PM_{2.5}$, (b) NO_x, (c) TVOCs correlation

References:

Duan, S., Jiang, N., Yang, L., Zhang, R.: Transport Pathways and Potential Sources of $PM_{2.5}$ During the Winter in Zhengzhou, Environmental Science, Jan 8;40(1):86-93, https://doi.org/10.13227/j.hjkx.201805187, 2019.

8. Line 222-223: "[…] Among them, Case 1 (from December 5 to December 10 and […]" A closing bracket is missed.

Response**:** We have revised it in the manuscript.

9. Section 3.2 Source appointment

Line 272: 'indicating that the measured air VOC content was influenced by both remote sources and urban area emissions.', Are you referring to all VOCs? Or specifically to m/p-xylene and ethylbenzene?

Response**:** We apologize for the impact on your understanding due to our negligence. We are referring to m/p-xylene and ethylbenzene here.

10. Line 271-273: Your conclusion indicates that VOCs are influenced by transport and emissions from distant regions. Can this be further substantiated through transport or other means?

Response**:** We infer the photochemical age of the air mass by the ratio of X/E. When the ratio is significantly lower than 3, it indicates that VOC mainly migrates from long-distance sources (aged air masses) (Kumar et

al., 2018; Cerón Bretón et al., 2020). The average X/E value in this study was 2.0, indicating that the measured air VOCs content was affected by transport of nearby or long-distance source emissions.

To further confirm that VOCs are affected by long-range transport, we conducted a potential source analysis of VOCs.

The area covered by the airflow trajectory was gridded, and the 80th percentile values of TVOCs for each process were set as standard values to obtain a map of the potential source distribution of TVOCs. Areas with high PSCF values indicate potential source areas of VOCs pollution (Figure 6).

Figure 6 (a) shows the potential source analysis of VOCs during the infection period. The areas with the highest PSCF values (> 0.36, red) are found in Jincheng and Xi'an, northwest of Zhengzhou, and the areas with high PSCF values (> 0.28, orange) include Luoyang, Jiyuan, and north of Xuchang, which are all industrial-intensive cities. Figure 5 (b) shows the results of the recovery period, with a wider distribution of potential sources than the former, and a greater variation in the areas of high PSCF values. Compared with the previous month, Handan and Liaocheng areas become new high PSCF areas, the influence of Xi'an is weakened, and the yellow area (PSCF > 0.2) is shifted from the northwest to the northeast of Zhengzhou.

The above analysis can also show that the VOCs at the observation sites are mainly influenced by the transmission from the distant areas.

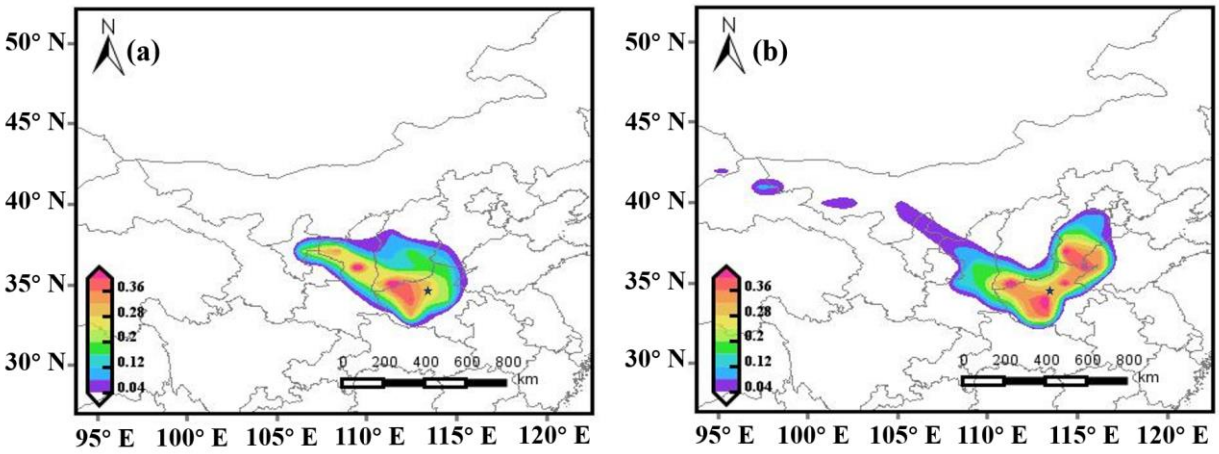


Figure 6. Potential source areas for VOCs (a) Infection period (b) Recovery period (Black pentagrams represent sampling locations)

Reference:

Cerón Bretón, J. G.: Health Risk Assessment of the Levels of BTEX in Ambient Air of One Urban Site Located in Leon, Guanajuato, Mexico during Two Climatic Seasons, Atmosphere, 11, 165, https://doi.org/10.3390/atmos11020165, 2020.

Kumar, A., Singh, D., Kumar, K., Singh, B. B., and Jain, V. K.:

Distribution of VOCs in urban and rural atmospheres of subtropical India: Temporal variation, source attribution, ratios, OFP and risk assessment, Science of the Total Environment, 613-614, 492-501, https://doi.org/10.1016/j.scitotenv.2017.09.096, 2018.

11. Line 306: 'olefins' should be corrected to 'alkenes'.

Response**:** We have modified it in the revised version.

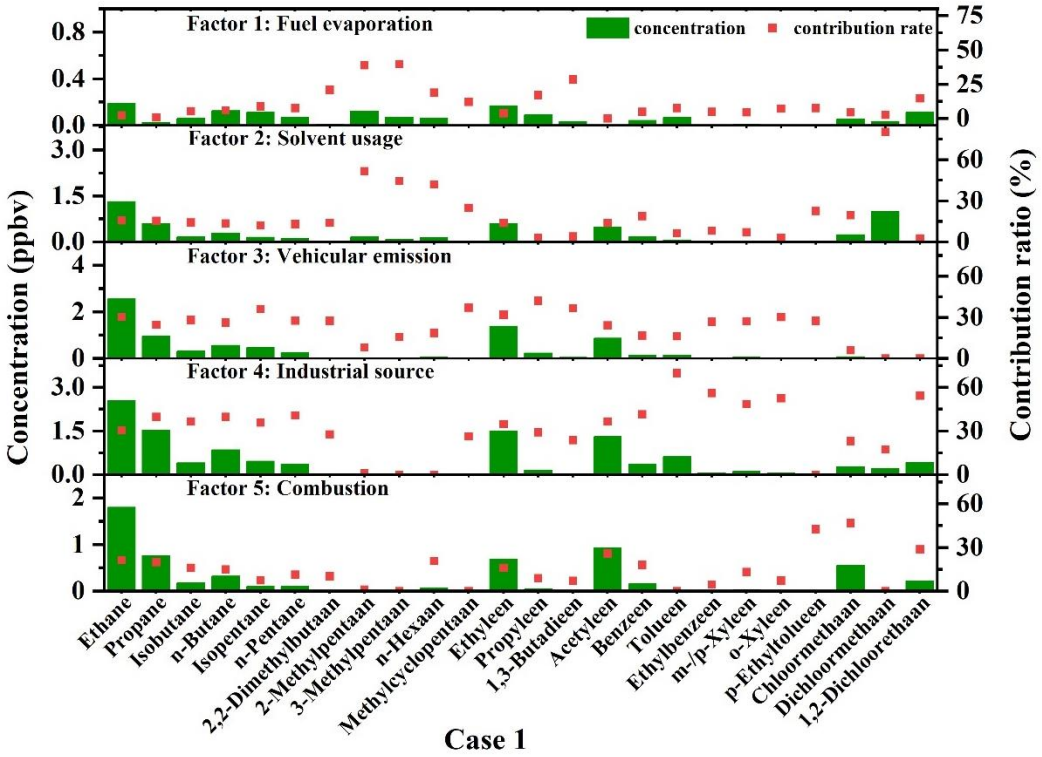
12. Line 316-325: Have you performed PMF in Case 1, Case 3, and clean days? It is recommended to check whether the results of factor analysis are consistent in different conditions (Case 1, Case 2, and clean days) and compare the results.

Response**:** We have indeed performed PMF on infection period, recovery period, Case 1, Case 2 and clean days.

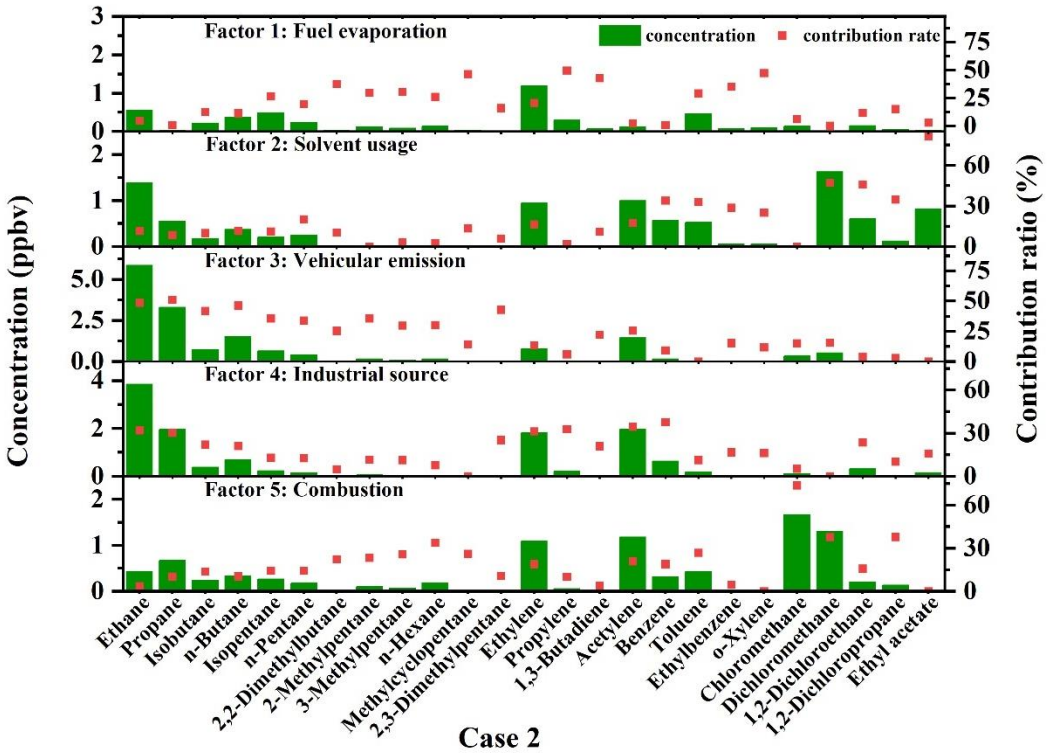
The PMF results for infection period (Dec 1 to 30, 2022), and recovery period (Jan 1 to 31), as well as the two pollution events and clean days, are shown in the figures below (Figure 7). They all exhibit the same 5 factors. It is worth noting that there are two y-axes in Figure 6: the left side represents the concentration of VOCs in units of ppbv, and the right side represents the percentage of specific VOCs within that factor.

Additionally, the concentration scales of some figures also differ.

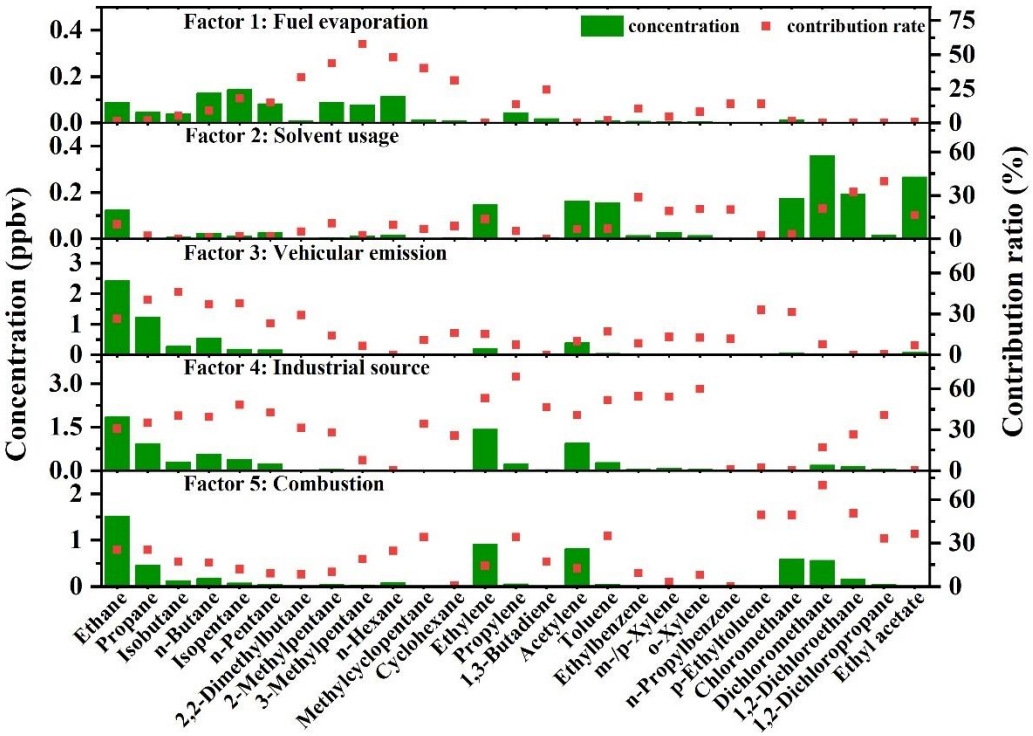
Concentrations of most species were significantly higher during the recovery period than during the infection period. The representative pollution processes in both periods showed the same results as well, with a 79% higher concentration of TVOCs in Case 2 (65.1 ppbv) compared to Case 1 (36.3 ppbv) (Figure 8). While in Case 1 industry was the dominant source of VOCs, by Case 2 motorized sources reached a concentration value of 21.2 ppbv, accounting for 33% of the observed VOCs, and became the dominant source of emissions. This is consistent with the fact that people's mobility activities have increased after the epidemic has entered the recovery period. As a group of VOCs species with the highest concentration share, ethane and propane contributed more to the clean day motor vehicle sources than other processes, which also resulted in a 34% clean day motor vehicle source share.


Factor 1: Fuel evaporation
concentration
contribution rate
Factor 2: Solvent usage
Factor 3: Vehicular emission
Factor 4: Industrial source
Factor 5: Combustion
Concentration (ppbv)
Contribution ratio (%)
Ethane
Propane
Isobutane
n-Butane
Isopentane
n-Pentane
2,2-Dimethylbutaan
2-Methylpentaan
3-Methylpentaan
n-Hexaan
Methylcyclopentaan
Ethyleen
Propyleen
1,3-Butadieen
Acetyleen
Benzeen
Tolueen
Ethylbenzeen
m-/p-Xyleen
o-Xyleen
p-Ethyltolueen
Chloormethaan
Dichloormethaan
1,2-Dichloorethaan

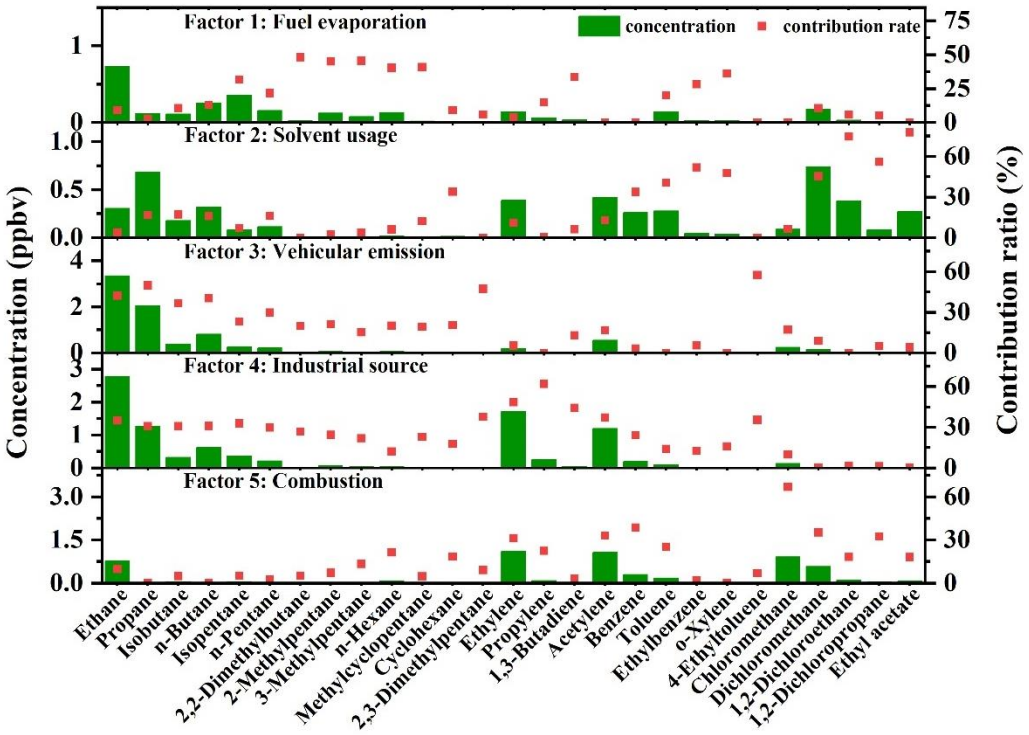
Case 1


Factor 1: Fuel evaporation
concentration
contribution rate
Factor 2: Solvent usage
Factor 3: Vehicular emission
Factor 4: Industrial source
Factor 5: Combustion
Concentration (ppbv)
Contribution ratio (%)
Ethane
Propane
Isobutane
n-Butane
Isopentane
n-Pentane
2,2-Dimethylbutane
2-Methylpentane
3-Methylpentane
n-Hexane
Methylcyclopentane
2,3-Dimethylpentane
Ethylene
Propylene
1,3-Butadiene
Acetylene
Benzene
Toluene
Ethylbenzene
o-Xylene
Chloromethane
Dichloromethane
1,2-Dichloroethane
1,2-Dichloropropane
Ethyl acetate

Case 2



infection period



recovery period

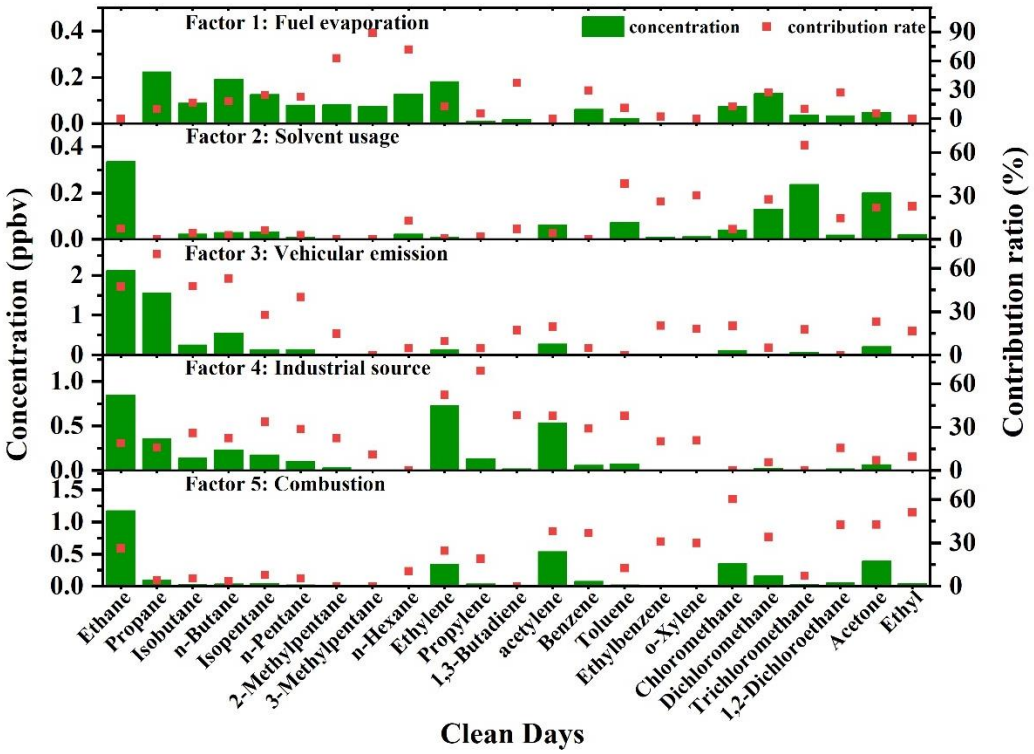


Figure 7. Infection period, recovery period, high pollution events, and clean days PMF source analysis

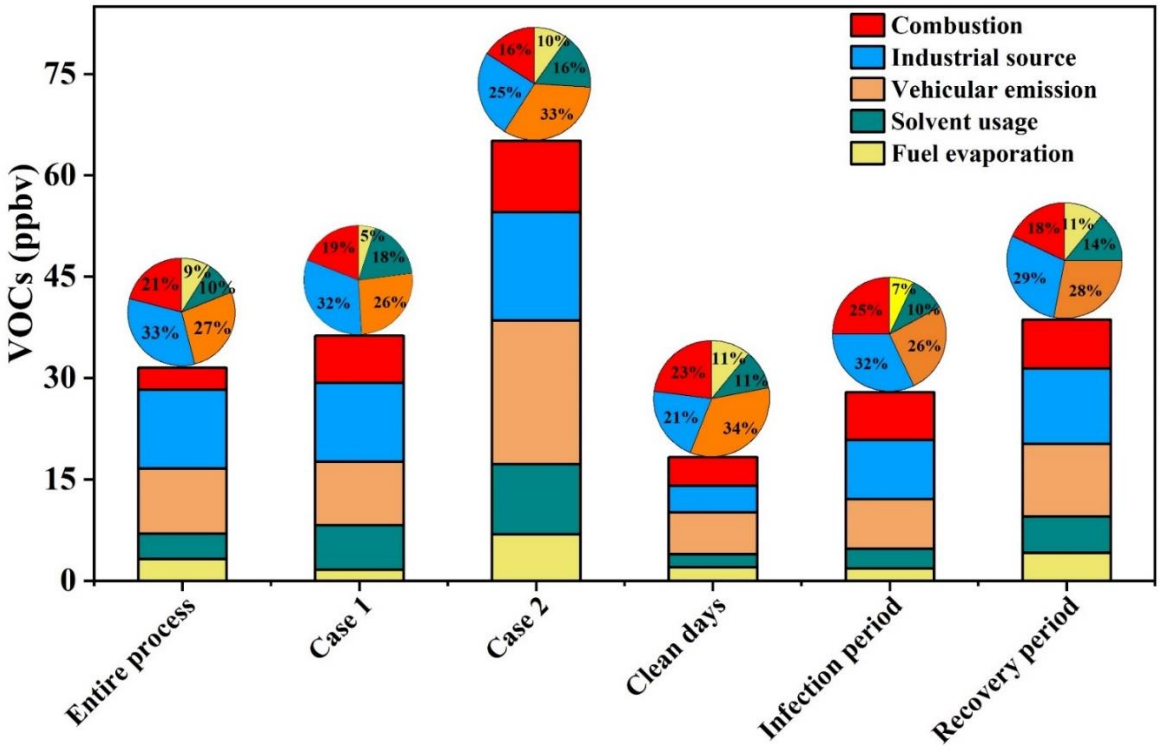


Figure 8. Contribution of each source to VOCs for different processes

13. Section 3.3 SOAFP

In this part, you only discuss the Case 1 and Case 2 processes, and you think that the control of $PM_{2.5}$ pollution in winter should focus on controlling vehicle emissions, solvent use, and combustion. I don't think it's convincing enough. It is recommended to add analysis of clean days. Contrast the pollution process with the clean day.

Response**:** VOCs are estimated to contribute about 16−30% or more of $PM_{2.5}$ by mass through SOA production (Huang et al., 2014). Therefore, by calculating the SOAP value, the influence of different sources on $PM_{2.5}$ production can be reflected to a certain extent.

We calculated the SOAP for the different processes from the PMF results in the previous question and added the results for the clean days as you suggested. The modified results are shown in Figure 9.

The SOAP of Case 2 was 65.6 μg/m^3, which was much higher than that of Case 1 (37.6 μg/m^3), and the main sources of SOAP differed significantly between the two pollution processes on the clean days. Industrial sources were absolutely dominant in Case 1 (63%). While in Case 2 the contribution of each pollution source is relatively more even, the

contribution of solvent use sources and fuel volatilization sources increases to 32% and 26% as the major SOAP sources. The result of clean day with SOAP of 8.8 μg/m^3 also shows that industrial and solvent use sources are the most dominant SOAP sources. Therefore, there is a need to reduce $PM_{2.5}$ pollution by controlling emissions from industrial and solvent use sources.

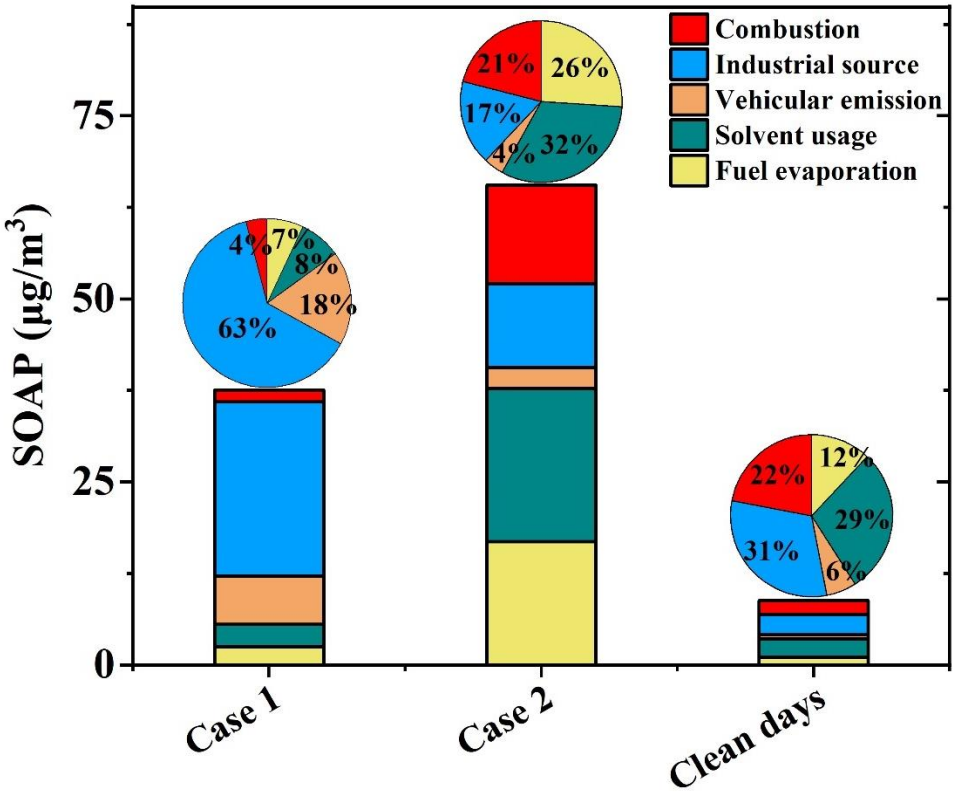


Figure 9. SOAP value and contribution ratio of each component

References:

Huang, R. J.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature 2014, 514 (7521), 218−22.