

The variations of VOCs based on the policy change of Omicron in traffic-hub city Zhengzhou

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Abstract: Online volatile organic compounds (VOCs) were monitored before and after the Omicron policy change at an urban site in polluted Zhengzhou from December 1, 2022, to January 31, 2023. The characteristics and sources of VOCs were investigated. The daily mean concentrations of PM_{2.5} and total VOCs (TVOCs) ranged from 53.5 to 239.4 $\mu\text{g}/\text{m}^3$ and 15.6 to 57.1 ppbv, respectively, with mean values of $111.5 \pm 45.1 \mu\text{g}/\text{m}^3$ and 36.1 ± 21.0 ppbv, respectively, throughout the period. Two severe pollution events (designated as Case 1 and Case 2) were identified in accordance with the National Ambient Air Quality Standards (NAAQS) (China's National Ambient Air Quality Standards (NAAQS) from 2012). Case 1 (December 5 to December 10, PM_{2.5} daily mean = 142.5 $\mu\text{g}/\text{m}^3$) and Case 2 (January 1 to January 8, PM_{2.5} daily mean = 181.5 $\mu\text{g}/\text{m}^3$) occurred during the infection period (when the policy of "full nucleic acid screening measures" was in effect) and the recovery period (after the policy was cancelled), respectively. The PM_{2.5} and TVOCs values for Case 2 are, respectively, 1.3 and 1.8 times higher than those for Case 1. The results of the positive matrix factor modeling demonstrated that the primary source of volatile organic compounds (VOCs) during the observation period was industrial emissions, which constituted 32% of the total VOCs, followed by vehicle emissions (27%) and combustion (21%). In Case 1, industrial emissions constituted the primary source of VOCs, accounting for 32% of the total VOCs. In contrast, in Case 2, the contribution of vehicular emission sources increased to 33% and became the primary source of VOCs. The secondary organic aerosol formation potential for Case 1 and Case 2 were found to be 37.6 $\mu\text{g}/\text{m}^3$ and 65.6 $\mu\text{g}/\text{m}^3$, respectively. In Case 1, the largest contribution of SOAP from industrial sources accounted for the majority (63%, 23.8 $\mu\text{g}/\text{m}^3$), followed by vehicular sources (18%).

34 After the end of the epidemic and the resumption of productive activities in the society,
35 the difference in the proportion of SOA generated from various sources decreased. Most
36 of the SOAP came from solvent use and fuel evaporation sources, accounting for 32%
37 (20.9 $\mu\text{g}/\text{m}^3$) and 26% (16.8 go/m^3), respectively. On days with minimal pollution,
38 industrial sources and solvent use remain the main contributors to SOA formation.
39 Therefore, regulation of emissions from industry, solvent-using industries and motor
40 vehicles need to be prioritized to control the $\text{PM}_{2.5}$ pollution problem.

41

42 **Keywords: Volatile organic compounds; Pollution episode; Source apportionment; Positive**
43 **Matrix Factorization model; Secondary organic aerosol formation potential;**

44 **1. Introduction**

45 Volatile organic compounds (VOCs) in the atmosphere have high reactivity and
46 can react with nitrogen oxides (NO_x) to form a series of secondary pollutants such as
47 ozone (O₃) and secondary organic aerosol (SOA), resulting in regional air pollution (Li
48 et al., 2019; Hui et al., 2020). The problem of O₃ pollution has been plaguing major
49 urban agglomerations in China (Zheng et al., 2010; Li et al., 2014; Wang et al., 2017).
50 SOA is an important component of fine particulate matter (PM_{2.5}) and contributes
51 significantly to haze pollution (Liu et al., 2019). PM_{2.5} remains the most significant air
52 pollutant in many Chinese cities for years (Shao et al., 2016; Wu et al., 2016). In
53 addition, VOCs, represented by the benzene homologues, can cause damage to kidneys,
54 liver, and nervous system of humans when they enter the body (Zhang et al., 2018).

55 Studies have shown that the most common VOC components in China are alkanes,
56 olefins, aromatic hydrocarbons, oxygenated VOCs (OVOCs), and halogenated
57 hydrocarbons, among which alkanes are the most abundant species (Liu et al., 2020;
58 Zhang et al., 2021a). VOCs in the atmosphere have a wide range of sources, and VOCs
59 in different regions are affected by multiple factors such as local geography, climate,
60 and human activities (Mu et al., 2023; Zou et al., 2023). The above reasons lead to
61 significant regional and seasonal differences in the characteristics of VOCs (Song et al.,
62 2021). For example, the annual average concentration of VOCs in the coastal
63 background area of the Pearl River Delta is 9.3 ppbv. The seasonal variation trend of
64 VOCs is high in autumn and winter and low in summer (Yun et al., 2021). In contrast,
65 the average VOC concentration in autumn and winter in Beijing was 22.6 ± 12.6 ppbv,
66 and the VOC concentration in the winter heating period was twice that in the autumn
67 non-heating period (Niu et al., 2022).

68 Moreover, the sources of VOC components in different regions are also related to
69 the local industrial structure and living habits. In rural areas of North China Plain in
70 winter, it is found that the SOA formation potential (SOAP) of VOCs under low NO_x
71 conditions is significantly higher than that under high NO_x conditions, and the increase
72 of aromatic hydrocarbon emissions caused by coal combustion is the main reason for
73 the higher SOAP in winter (Zhang et al., 2020). Li et al. (2022) found that the average
74 increased concentration of acetylene was 4.8 times from autumn to winter in the
75 Guanzhong Plain, indicating that fuel combustion during the heating period in winter
76 has a significant impact on the composition of VOCs. In contrast, continuous

77 observations conducted by Zhou et al. (2022) in the suburbs of Dongguan in summer
78 found that industrial solvent usage, liquefied petroleum gas (LPG) and oil and gas
79 volatilization were the main sources of VOCs. The results highlighted a wide variation
80 of characteristics, sources and chemical reactions of VOCs in the atmosphere thus it is
81 necessary to investigate VOCs in different cities when formulating control measures.

82 Zhengzhou, as the capital of Henan Province, is an important transportation hub
83 and economic center in the Central Plains region. Zhengzhou is currently facing
84 significant air pollution problems, with the Air Quality Index at the bottom of the
85 national ranking of 168 cities for many years. In January 2023, for example, the number
86 of polluted days with PM_{2.5} as the primary pollutant was 17, and the daily average value
87 of PM_{2.5} reached a maximum of 298 $\mu\text{g}/\text{m}^3$
88 ([https://www.aqistudy.cn/historydata/daydata.php?city=%E9%83%91%E5%B7%9E](https://www.aqistudy.cn/historydata/daydata.php?city=%E9%83%91%E5%B7%9E&month=202301)
89 &month=202301, Accessed Jan 2024), which is almost 300% higher than the Chinese
90 daily average standard (grade II, 75 $\mu\text{g}/\text{m}^3$). The studies of VOCs were carried out in
91 Zhengzhou in recent years, which focused on the characteristics and sources of VOCs
92 during pollution episodes (Lai et al., 2024) or before the coronavirus epidemic outbreak
93 (Li et al., 2020; Zhang et al., 2021b). While some atmospheric VOCs studies involving
94 the impact of Covid-19 lockdown have been performed in India (Singh et al., 2023a),
95 in China (e.g., Pei et al., 2022; Jensen et al., 2023; Zuo et al., 2024), or with respect to
96 toluene, benzene, m/p-xylene and ethylbenzene only (e.g., Sahu et al., 2022; Singh et
97 al., 2023b), a gap persisted in the investigation of VOCs due to the impact of
98 abolishment of China's zero-policy. Furthermore, some studies have discussed the
99 impact of changes in human production activities on air pollution during and after the
100 outbreak of the coronavirus disease (e.g., Ma et al., 2022; Jiang et al., 2023; Song et al.,
101 2023), but as mentioned earlier, only a few studies with in-depth exploration of the
102 changes in VOCs and none dealing with ending the zero-Covid policy during Omicron
103 variant infection period.

104 In this study, we conducted continuous online observations of VOCs during the
105 polluted winter season at an urban site in Zhengzhou. The study covered the period
106 following the removal of lockdown measures. We focused on pollution events when the
107 daily average PM_{2.5} concentration exceeded 75 $\mu\text{g}/\text{m}^3$ (China's Class II standard) for
108 more than three consecutive days. Days with PM_{2.5} concentrations below 35 $\mu\text{g}/\text{m}^3$
109 (China's Class I standard) were classified as clean days. During this period, China lifted
110 zero-COVID strategies, announcing the '10 measures' for optimizing COVID-19 rules

111 on December 7, 2022 (http://www.news.cn/politics/2022-12/07/c_1129189285.htm,
112 Accessed Jan 2024). Zhengzhou's epidemic prevention and control measures changed
113 with the issuance of Circular No. 163 on December 4, 2022, which allowed the
114 reopening of closed public places. As a result, movement within Zhengzhou increased
115 and social production resumed. Our research specifically examines the period
116 dominated by the COVID-19 Omicron variant. where they demonstrate notable
117 differences from the early virus strains (i.e., original SARS-CoV-2 virus and Delta) in
118 terms of geographical transmission, the scale of the infected population, and symptom
119 manifestation (Petersen et al., 2022; Merino et al., 2023).

120 After the quarantine policy was lifted, people basically rested at home due to
121 infection or fear of infection with Omicron. The resumption of normal production and
122 life depends on herd immunization. This outbreak event is the longest in duration and
123 the largest in number of infections since the 2020 outbreak of the novel coronavirus in
124 Zhengzhou. It would be beneficial to investigate the impact of this event on emissions
125 related to transportation and industrial production. This change is worth exploring in
126 terms of its impact on transportation and industrial production emissions. Therefore,
127 the characteristics and variations of VOCs during different periods were investigated to
128 assess their impact on the formation of SOA and to provide data support for future
129 pollution control policies in Zhengzhou.

130

131 **2. Materials and methods**

132 **2.1 Sample collection and Chemical analysis**

133 The online VOCs observation station is located on the roof of the Zhengzhou
134 Environmental Protection Monitoring Center, which is in the urban area. The sampling
135 site is close to main roads on three sides (150 m away from Funiu Road on the east side,
136 200 m away from Qinling Road on the west side, and connected to Zhongyuan Road
137 on the south side), and surrounded by residential areas and commercial areas without
138 other large nearby stationary sources. The sampling period for this study was from
139 December 1, 2022, to January 31, 2023, and serious PM_{2.5} pollution in Zhengzhou was
140 of frequent occurrence during December and January.
141 ([https://www.aqistudy.cn/historydata/monthdata.php?city=%e9%83%91%e5%b7%9e](https://www.aqistudy.cn/historydata/monthdata.php?city=%e9%83%91%e5%b7%9e#:~:text=%E7%94%9F%E5%91%BD%E6%9D%A5%E6%BA%90%E8%87%AA%E7%84%B6%EF%BC%8C%E5%81%A5)
142 [#:~:text=%E7%94%9F%E5%91%BD%E6%9D%A5%E6%BA%90%E8%87%AA%](https://www.aqistudy.cn/historydata/monthdata.php?city=%e9%83%91%e5%b7%9e#:~:text=%E7%94%9F%E5%91%BD%E6%9D%A5%E6%BA%90%E8%87%AA%E7%84%B6%EF%BC%8C%E5%81%A5)
143 [E7%84%B6%EF%BC%8C%E5%81%A5](https://www.aqistudy.cn/historydata/monthdata.php?city=%e9%83%91%e5%b7%9e#:~:text=%E7%94%9F%E5%91%BD%E6%9D%A5%E6%BA%90%E8%87%AA%E7%84%B6%EF%BC%8C%E5%81%A5)). Apart from a brief occurrence of rain and
144 snow on December 25, the sampling days were either sunny or cloudy. The wind speed
145 (WS), temperature (Temp) and relative humidity (RH) during this period were 1.3 ± 0.9
146 m/s, 5.3 ± 3.2 °C and $38.9 \pm 19.0\%$), respectively, similar to the values observed in
147 previous years in Zhengzhou. It is interesting to point out that the sampling period in
148 the present study covered the entire infection period of Omicron in Zhengzhou,
149 including the phase of surge in infected population (Infection period, from 2022.12.01
150 to 2022.12.31) and restoration of production and livelihood phase (Recovery period,
151 from 2023.1.1 to 2023.1.31 in 2023) (Fig. S1, Chinese Center for Disease Control and
152 Prevention, 2023).

153 The VOCs were measured hourly using a GC-FID/MS (TH-PKU 300 b, Wuhan
154 Tianhong Instruments Co., China). The instrument TH-PKU300b includes electronic
155 refrigeration ultra-low temperature pre-concentration sampling system, analysis system
156 and system control software. The ambient VOCs in the first 5 minutes of each hour
157 were collected by the sampling system and then entered the concentration system.
158 Under low temperature conditions, the VOCs samples collected were frozen in the
159 capillary capture column, and then quickly heated and resolved, so that the compounds
160 entered the analysis system. After separation by chromatographic column, the
161 compounds were monitored by FID and MS detectors. During the detection process,
162 the atmospheric samples collected undergo analysis through two distinct pathways. C2-
163 C5 hydrocarbons are analyzed using FID, while C5-C12 hydrocarbons, halocarbons,

164 and OVOCs are analyzed with a MS detector. After excluding species with missing data
165 exceeding 10%, the detected volatile organic compounds include 29 alkanes, 11 alkenes,
166 17 aromatics, 35 halocarbons, 12 OVOCs, 1 alkyne (acetylene), and 1 sulfide (CS₂)
167 with a total of 106 compounds. A detailed description of the instrumentation can be
168 found in our previous study (Zhang et al., 2021b; Shi et al., 2022; Zhang et al., 2024).

169 The instrument was calibrated per week to ensure the accuracy of VOCs by
170 injecting standard gases with a five-point calibration curve. The detection limit of C2-
171 C5 hydrocarbons ranges from 0.007 to 0.099 ppbv, other hydrocarbons are 0.004–0.045
172 ppbv, halogenated hydrocarbons 0.009-0.099 ppbv, OVOCs and other compounds of
173 0.006–0.095 ppbv. Thirty-two of the monitored VOCs had over 90% observed data
174 greater than the detection limit, and 34 had more than 50% observed data greater than
175 the detection limit.

176 Simultaneous observations at the same site were also carried out for particulate
177 matter (PM_{2.5}, PM₁₀), other trace gases (carbon monoxide (CO), O₃, nitric oxide (NO),
178 nitrogen dioxide (NO₂)), and meteorological data (Temperature, RH, WS, and wind
179 direction (WD)) based on 1 h resolution.

180 **2.2 Positive Matrix Factorization (PMF) model**

181 EPA PMF5.0 model was used for the quantitative source analysis of VOCs (Norris
182 et al., 2014). The principles and methods have been described in detail in previous
183 studies (Mozaffar et al., 2020; Zhang et al., 2021b). The decomposition of the PMF
184 mass balance equations is simplified as follows (Norris et al., 2014):

185

$$186 \quad x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

187

188 where x_{ij} is the mass concentration of species j measured in sample i ; g_{ik} is the
189 contribution of factor k to the sample i ; f_{kj} represents the content of the j th species in
190 factor k ; e_{ij} is the residual of species j in sample i ; p represents the number of factors.

191 The fitting objective of the PMF model is to minimize the function Q to obtain the
192 factor contributions and contours. The formula for Q is given in Eq. (2):

193

194
$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (2)$$

195

196 where n and m denote the number of samples and VOC species, respectively.

197 Concentrations and uncertainty data are required for the PMF model. In this study,
 198 the median concentration of a given species is used to replace missing values with an
 199 uncertainty of four times of the median values; data less than the Method Detection
 200 Limit (MDL) were replaced with half the MDL, with an uncertainty of 5/6 of the MDL;
 201 and the uncertainty for values greater than the MDL was calculated using Eq. (3). In
 202 Eq. (3), EF is error fraction, expressed as the precision of VOCs species, and the setting
 203 range can be adjusted from 5 to 20% according to the concentration difference (Buzcu
 204 et al., 2006; Song et al., 2007); and c_{ij} is the concentration of species j in sample i :

205
$$U_{ij} = \sqrt{(EF \times c_{ij})^2 + (0.5 \times MDL)^2} \quad (3)$$

206 when the concentration of VOCs in the species is less than the value of the
 207 detection limit U_{ij} is calculated using Eq. (4):

208
$$U_{ij} = \left(\frac{5}{6}\right) MDL \quad (4)$$

209 VOC species and concentration input into PMF were carefully selected to ensure
 210 the accuracy of the PMF results. Species were excluded when over 25% of the samples
 211 were missing or concentrations values were below the MDL (Gao et al., 2018); VOCs
 212 with a short lifetime in the atmosphere were also excluded unless they are source-
 213 relative species (Zhang et al., 2014; Shao et al., 2016). After that, retained VOC species
 214 were categorized according to the signal-to-noise ratio (S/N) with $S/N < 0.2$ species
 215 categorized as bad, $0.2 < S/N < 2$ species categorized as weak; and $S/N > 2$ species
 216 categorized as strong (Shao et al., 2016).

217 We used displacement of factor elements (DISP) to assess PMF modelling
 218 uncertainty (for a description, see Paatero et al. (2014)). Q was less than 1% and no
 219 swaps occurred for the small est dQ^{\max} in DISP. F_{peak} values from -2 to 2 were tested
 220 to explore the rotational stability of the solutions. $Q_{\text{true}}/Q_{\text{exp}}$ is lowest when $F_{\text{peak}} = 0$,
 221 so we chose the PMF results for that case (Fig. S2a). After examining 3-8 factors, 20
 222 base runs with 5 factors eventually selected to represent final result. We provide an
 223 explanation of factor selection in the supplementary materials. Fig. S2(b) includes
 224 $Q_{\text{true}}/Q_{\text{exp}}$, $Q_{\text{robust}}/Q_{\text{exp}}$ for factors 3-8. The slopes of these two ratios in changed at five

225 factors, and we found that five factors were more realistic after repeated comparisons
226 of the results at four, five and six factors.

227 **2.3 SOA generation potential**

228 The contributions of VOC species to SOAP were calculated based on the toluene
229 weighted mass contributions (TMC) method (Derwent et al., 2010). The methodology
230 for calculating SOAP is as follows:

231

$$232 \text{SOAPF}_i = \frac{\text{VOCs component } i \text{ to SOA mass concentration increments}}{\text{Toluene to SOA mass concentration increment}} \times 100 \quad (5)$$

233

234 SOAPF_i for each VOC is taken from the literature (Derwent et al., 2010). The
235 SOAP was estimated by multiplying the SOAPF_i value by the concentration of
236 individual VOC species. The SOAP calculations through each VOC are as follows:

237

$$238 \text{SOAP} = \sum E_i \times \text{SOAPF}_i \quad (6)$$

239 E_i is the concentration of species i .

240

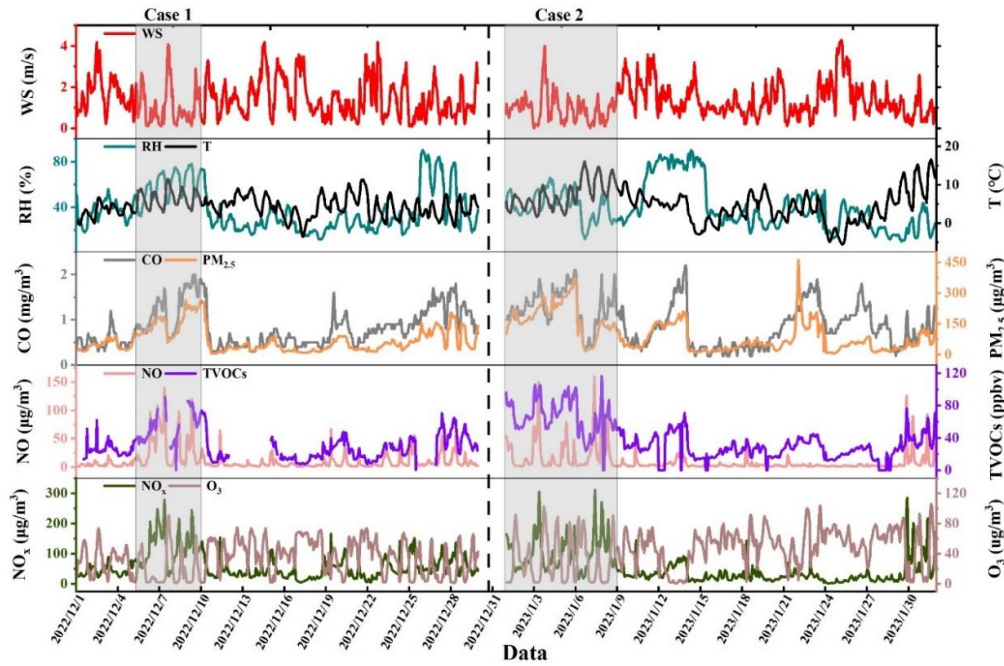
241 **3. Results and discussion**

242 **3.1 Overview of variation in pollutants and meteorological** 243 **parameters**

244 Figure 1 shows the time series of meteorological parameters, TVOCs, O₃, NO_x,
245 SO₂, CO and PM_{2.5} during the observed periods. Low WS and Temperature were found
246 with an average value of 1.3 ± 0.6 m/s and 5.0 ± 2.5 °C, respectively, during the entire
247 period, comparable with observations at the same site in 2021 (Lai et al., 2024). A total
248 of 62 days of valid data was acquired with the daily average concentration of PM_{2.5}
249 ranging from 53 to 239 $\mu\text{g}/\text{m}^3$, with the average value of 111 ± 45 $\mu\text{g}/\text{m}^3$. The
250 concentration of TVOCs ranged from 15.6 to 57.1 ppbv with an average of 36.1 ± 21.0
251 ppbv, higher than the same period in last year (27.9 ± 12.7 ppbv, Lai et al., 2024).
252 During the observation period, the average values of T, WS and RH were 5.0 ± 2.5 °C,
253 1.3 ± 0.6 m/s and $38.9 \pm 16.7\%$, respectively.

254 Previous studies have shown that meteorological factors such as low WS, high RH,

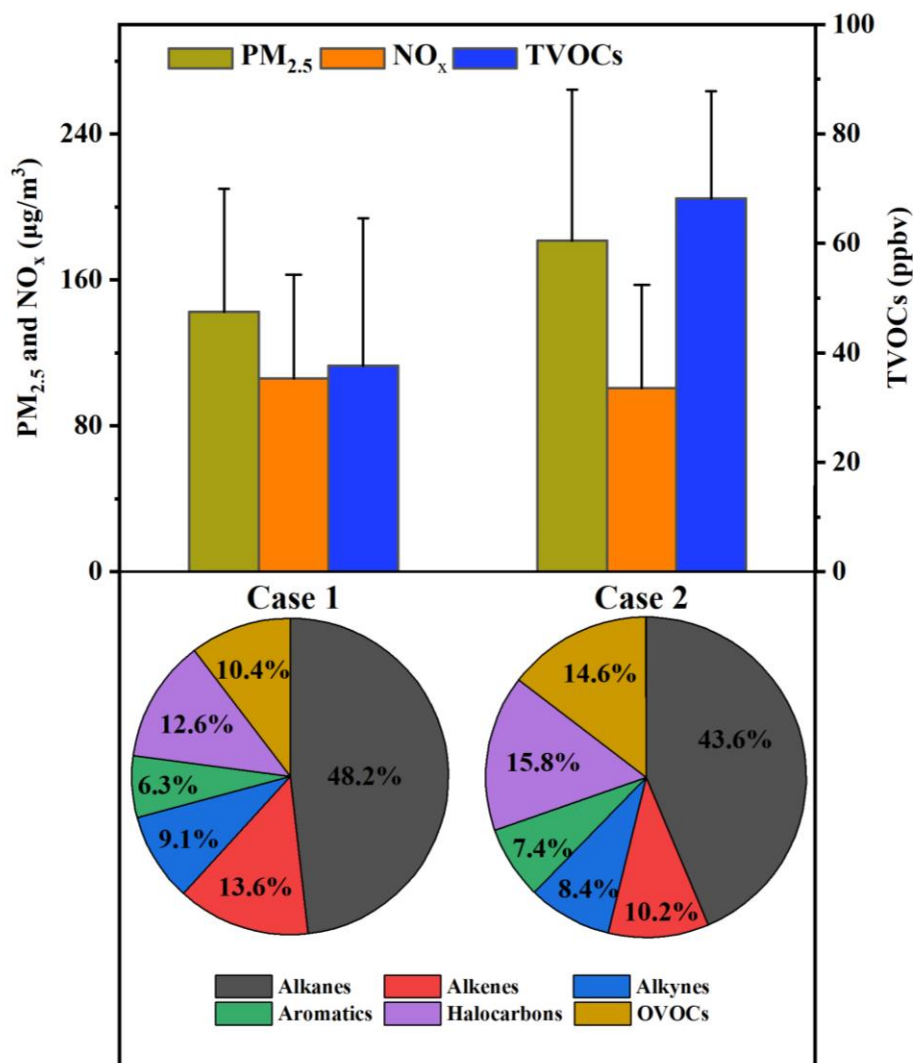
255 and low precipitation are responsible for the increase in PM_{2.5} pollution in Zhengzhou
256 in winter (Duan et al., 2019). Our analysis of the correlation between different
257 pollutants and meteorological conditions during the pollution period showed that
258 PM_{2.5}, TVOCs and NO_x were positively correlated with relative humidity (Fig. S3),
259 which is consistent with the results of some previous studies (Wang et al., 2019). Yu
260 et al. (2018) identified RH and WS as the most influential meteorological conditions
261 of PM_{2.5} during winter. Their findings revealed a positive correlation between hourly
262 PM_{2.5} concentrations and RH ($r = 0.84$, $p < 0.01$) and a negative correlation between
263 PM_{2.5} concentrations and WS ($r = -0.62$, $p < 0.01$). In this study, the WS on clean days
264 (1.4 ± 0.8 m/s) was higher than in Case 1 (1.2 ± 0.9 m/s) and Case 2 (0.9 ± 0.7 m/s),
265 while the RH was lower by 26.2% and 12.5% compared to Case 1 and Case 2,
266 respectively. These findings indicate that high RH and low WS significantly influence
267 the occurrence of pollution during the observation period. However, the mean PM_{2.5}
268 concentration during the recovery period was found to be 1.6 times higher than that
269 observed during the infection period. Furthermore, the concentrations of other
270 pollutants (including SO₂, NO₂, CO, and O₃) exhibited analogous trends during the
271 infection and recovery periods. The concentration of TVOCs during the recovery
272 period was 1.2 times higher than that during the infection period, exhibiting a
273 significant upward trend following the resumption of production. It is notable that WS,
274 which is only 0.3 m/s higher in Case 1 than in Case 2, and RH, which is 13% higher
275 in Case 1 than in Case 2, were relatively stable, while the concentration of pollutants
276 is significantly higher in Case 2 than in Case 1. This is presumably attributable to the
277 resumption of production activities in Case 2, which resulted in a notable increase in
278 emissions. Decreased trends of air pollutants were found in other studies before and
279 after the outbreak of the novel coronavirus (COVID-19) in early 2020 (Qi et al., 2021;
280 Wang et al., 2021).



281

282 Fig. 1. Time series of WS, T, RH, CO, PM_{2.5}, NO, TVOCs, NO_x and O₃ during the observation
 283 period.

284 The shadow section in Fig. 1 represents two haze pollution events during the
 285 monitoring period. A pollution event is determined when the daily average
 286 concentration of PM_{2.5} exceeds 75 µg/m³ (China's II-level standard) for at least three
 287 consecutive days. Case 1 (December 5 to December 10 with daily average PM_{2.5} =
 288 142.5 µg/m³) and Case 2 (January 1 to January 8 with daily average PM_{2.5} = 181.5
 289 µg/m³) were selected as they represent the pollution events in infection and recovery
 290 periods, respectively, due to their long duration and high pollution levels. Any day with
 291 a PM_{2.5} concentration lower than 35 µg/m³ (China's I-level standard) is considered as
 292 Clean day.



293
 294 Fig. 2. The concentration of PM_{2.5}, NO_x, TVOCs and the composition ratio of VOCs in Case 1 and
 295 Case 2.

296 As for the two representative pollution processes (Case 1 during the infection
 297 period and Case 2 during the recovery period), the concentration of TVOCs in Case 1
 298 and Case 2 were 48.4 ± 20.4 and 67.6 ± 19.6 ppbv (Fig. 2), respectively, increased by
 299 63% and 188% compared with values during clean days. The average concentrations
 300 of PM_{2.5} and TVOCs during Case 2 were 1.3 and 1.8 times the values in Case 1. The
 301 highest volume contributions of alkanes were found both in Case 1 (48%) and Case 2
 302 (44%), consistent with the results in the Yangtze River Delta region (36-43%, Liu et al.,
 303 2023). While alkenes exhibited higher volume percentages of 13% in Case 1, followed
 304 by halogenated hydrocarbon (12%) and OVOCs (10%). Higher volume percentages of
 305 alkanes and alkenes in Case 1 were similar to the results in the gasoline evaporation
 306 site in winter (Niu et al., 2022). Equivalent volume contribution of halogenated
 307 hydrocarbon and OVOCs (15%) were found in Case 2, followed by alkenes (10%).

308 Although aromatic hydrocarbons have the lowest volumetric contribution (6% in Case
 309 1 and 7% in Case 2), they show the largest increase from clean days to pollution.

310 Table 1 The average concentrations of meteorological parameters and pollutants during different
 311 processes.

Category	Entire process (2022.12.1- 2023.1.31)	Infection period (2022.12.1- 2022.12.31)	Recovery period (2023.1.1- 2023.1.31)	Case 1 (2022.12.5- 2022.12.10)	Case 2 (2023.1.1- 2023.1.8)	Clean Days
	N = 62 days	N = 31 days	N = 31 days	N = 6 days	N = 8 days	N = 8 days
WS (m/s)	1.3 ± 0.6	1.4 ± 0.6	1.3 ± 0.6	1.2 ± 0.9	0.9 ± 0.7	1.4 ± 0.8
T (°C)	5.0 ± 2.5	4.7 ± 1.7	5.4 ± 3.1	6.1 ± 2.2	7.4 ± 3.5	4.1 ± 3.0
RH (%)	38.9 ± 16.7	37.6 ± 15.5	40.2 ± 18.2	55.7 ± 14.7	42.0 ± 12.1	29.5 ± 18.1
TVOCs (ppbv)	36.1 ± 21.0	31.9 ± 18.1	39.8 ± 22.4	37.6 ± 27.0	68.2 ± 19.6	22.7 ± 11.1
SO ₂ (µg/m ³)	11.4 ± 2.7	10.2 ± 2.8	12.7 ± 2.3	11.0 ± 3.7	16.2 ± 6.1	6.5 ± 2.5
NO ₂ (µg/m ³)	47.2 ± 10.0	46.8 ± 8.6	47.8 ± 11.7	62.7 ± 20.5	65.0 ± 21.3	20.8 ± 15.9
CO (mg/m ³)	0.9 ± 0.2	0.8 ± 0.2	1.1 ± 0.2	1.2 ± 0.5	1.3 ± 0.4	0.5 ± 0.2
O ₃ (µg/m ³)	34.9 ± 6.0	31.1 ± 4.5	39.0 ± 4.6	21.8 ± 23.7	32.5 ± 29.6	52.6 ± 18.4
PM _{2.5} (µg/m ³)	111.5 ± 45.1	86.6 ± 34.6	138.3 ± 39.6	142.5 ± 67.4	181.5 ± 82.7	23.8 ± 16.8

312 Table 2 Concentration of VOC species during different processes (ppbv).

Category	Entire process	Infection period	Recovery period	Case 1	Case 2	Clean days
TVOCs	36.1 ± 21.0	31.9 ± 18.1	39.8 ± 22.4	48.4 ± 20.4	67.6 ± 19.6	17.5 ± 9.5
alkanes	16.8 ± 9.2	15.0 ± 8.4	18.4 ± 9.5	23.1 ± 10.0	29.5 ± 8.4	9.2 ± 5.6
alkenes	4.1 ± 2.7	3.8 ± 2.6	4.4 ± 2.7	6.5 ± 2.9	7.0 ± 2.6	1.7 ± 1.3
alkynes	3.1 ± 2.0	2.7 ± 1.7	3.4 ± 2.1	4.3 ± 2.0	5.8 ± 1.9	1.3 ± 0.8
aromatics	2.1 ± 2.0	1.8 ± 1.5	2.3 ± 2.2	3.0 ± 1.8	4.9 ± 2.8	0.7 ± 0.5
halogenated hydrocarbon	5.4 ± 3.3	4.4 ± 2.3	6.2 ± 3.8	6.0 ± 1.9	10.7 ± 3.6	2.7 ± 1.4
OVOCs	4.6 ± 3.2	3.5 ± 2.7	5.1 ± 3.5	5.0 ± 2.4	9.7 ± 2.8	1.9 ± 1.1

313 3.2 Source Analysis of VOCs

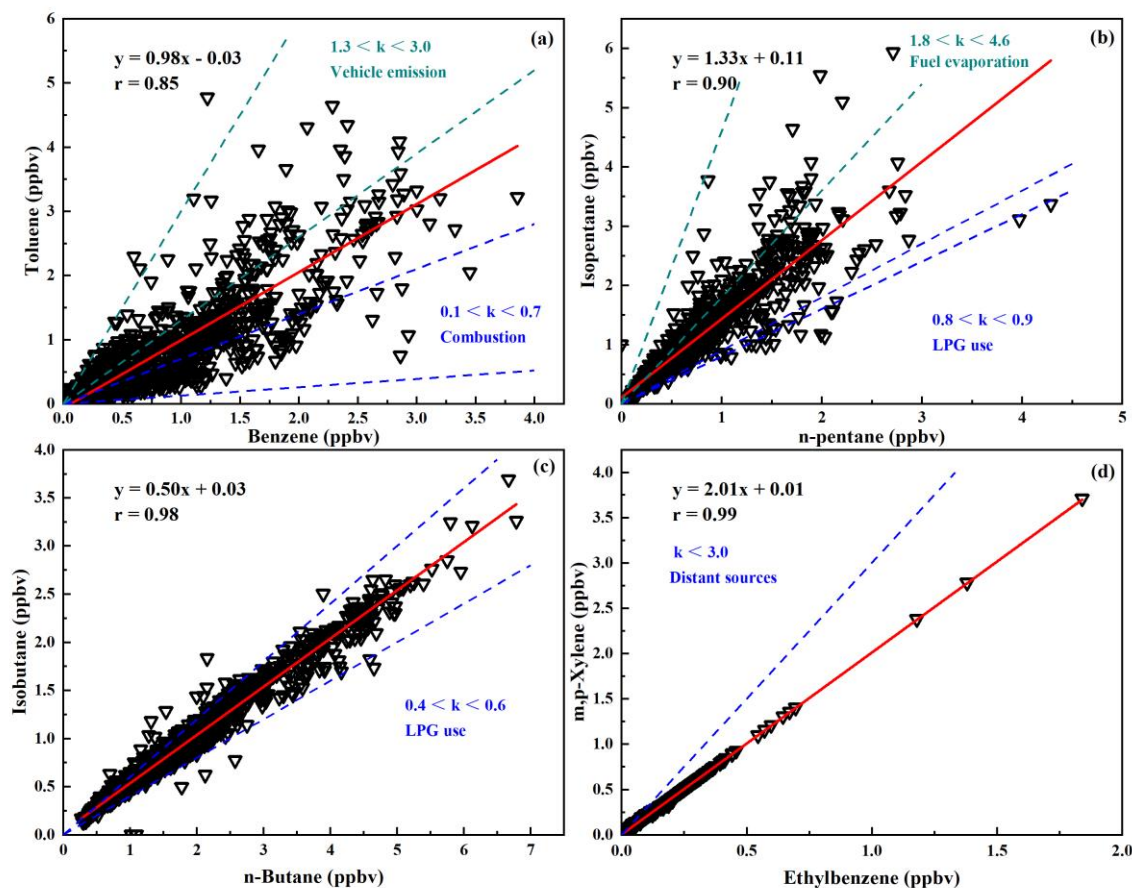
314 Specific VOC ratios can be used for initial source identification of VOCs and
 315 determination of photochemical ages of air masses (Monod et al., 2001; An et al., 2014;
 316 Li et al., 2019). In this study, the ratios of toluene/benzene (T/B), isopentane/n-pentane,
 317 isobutane/n-butane, and m/p-xylene/ethylbenzene (X/E) were selected to initially
 318 identify the potential sources of VOCs (Fig. 3). Concentrations of selected pollutants
 319 and ratios used are shown in Table S1.

320 The toluene-to-benzene ratio (T/B ratio) was widely used to assess the relative
321 importance of different sources. Specifically, T/B ratio with a value of 1.3-3.0 was
322 observed in vehicle emissions for vehicles with different fuel types (Schauer et al., 2002;
323 Wang et al., 2015). The reported T/B ratio for combustion processes was between 0.13
324 and 0.7 (Li et al., 2011; Wang et al., 2014). The mean value of T/B ratio for the entire
325 period was 1.0, with the majority of the data (99%) falling between 0.1 and 3.0 and
326 concentrated within the 0.7-1.3 range (49%). This suggests that both traffic emissions
327 and combustion **may be** significant sources of VOCs.

328 The isopentane/n-pentane concentration ratios of 0.6-0.8 represent mainly coal
329 combustion emissions, ratios of 0.8-0.9 represent LPG emissions, 2.2-3.8 represent
330 vehicle exhaust emissions, and 1.8-4.6 represent fuel evaporation (Conner et al., 1995;
331 Liu et al., 2008; Li et al., 2019). The sources of isopentane and n-pentane in this study
332 were intricate and multifaceted. The mean isopentane/n-pentane ratio was 1.4, with the
333 majority of data points (99%) falling within the range of 0.1-4.6, with a notable
334 concentration in the 0.8 to 1.8 interval. **This indicates that pentane is susceptible to a
335 combination of LPG emissions and fuel evaporation. It should be noted that this
336 analytical approach is not without limitations. For instance, the proportionality of
337 pentane may be influenced by a combination of LPG emissions and fuel evaporation.
338 Consequently, an in-depth examination of the sources of VOCs was conducted using
339 the PMF model in the next section.**

340 Isobutane/n-butane concentration ratios of 0.2-0.3 represent vehicle emissions,
341 0.4-0.6 represent LPG usage, and 0.6-1.0 represent natural gas emissions (Russo et al.,
342 2010; Zheng et al., 2018). The mean isobutane/n-butane ratio in this study was 0.5, with
343 the majority of data points (99%) falling within the 0.4-0.6 range, indicating that VOCs
344 at the observation sites were significantly influenced by the use of LPG. (Shao et al.,
345 2016; Zeng et al., 2023).

346 The ratio of X/E can be used to infer the photochemical age of the air mass. X/E
347 ratios around 2.5-2.9 are typical of urban areas, indicating that VOCs are mainly from
348 the urban area (fresh air mass) (Kumar et al., 2018). When this ratio is significantly
349 lower than 3.0, it indicates that VOCs are mainly transported from distant sources
350 (aging air masses) (Kumar et al., 2018). The average X/E value in this study was 2.0
351 (Fig. 3(d)), indicating low photochemical activity and aging of the air mass at the
352 observation site. Potential source analyses also indicate that air masses are affected by
353 long-range transport (Fig. S4).



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Fig. 3. Correlation analysis between specific VOC species.

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Figure 4 shows the chemical profiles of individual VOCs resolved by the PMF model during the entire observation period. 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. These 5 factors have been commonly reported before, e.g., in Shijiazhuang, northern China (Guan et al, 2023) and in Beijing (Cui et al., 2022).

362

Alkanes of C4-C6 substances were predominant in factor 1, including 2-methylpentane, 3-methylpentane, isobutane, n-butane, isopentane and n-pentane from oil and gas (Xiong et al., 2020). Fig. S5 shows that emissions from this source peak at midday, when fuel volatilization is high, The CPF plot shows that south-east is the dominant direction at wind speeds of less than 2 m/s (Fig. 5a). Therefore, factor 1 was identified as the source of oil and gas volatilization.

368

The contribution of benzene, toluene, methylene chloride, 1,2-dichloroethane and ethyl acetate was high in factor 2. It has been shown that benzene, toluene, ethylbenzene, and xylene is an important component in the use of solvents (Li et al., 2015); methylene

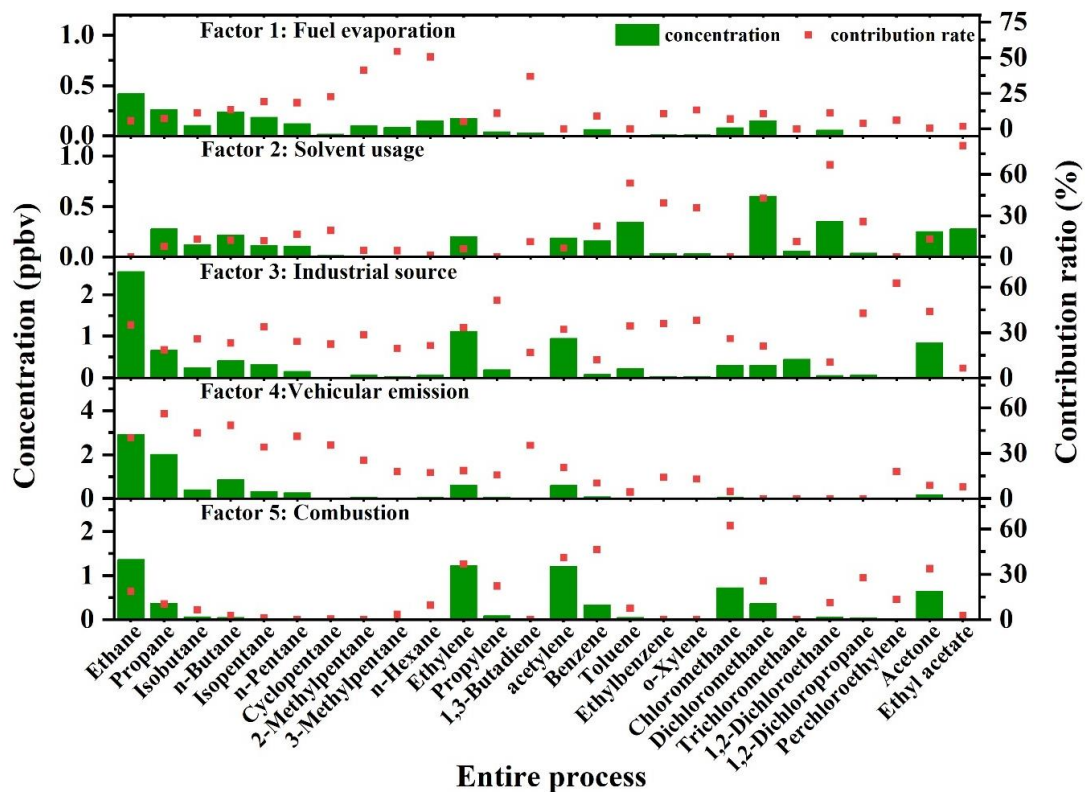
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371 chloride is often used as a chemical solvent, while esters are mostly used as industrial
372 solvents or adhesives (Li et al., 2015). Factor 2 is determined to be solvent usage source.
373 The CPF plot shows that due east is the main emission direction at wind speeds less
374 than 2 m/s and southeast is the main source at wind speeds greater than 2 m/s (Fig. 5b).

375 Factor 3 contains predominantly C3-C8 alkanes, olefins and alkynes, and
376 relatively high concentrations of benzene. These substances are usually emitted by
377 industrial processes (Shao et al., 2016), so Factor 4 is defined as an industrial source.
378 The CPF plots indicate that a local source at low wind speeds is the dominant sources
379 (Fig. 5c).

380 Factor 4 is characterized by relatively high levels of C2-C6 low-carbon alkanes
381 (ethane, propane, isopentane, n-pentane, isobutane and n-butane), olefins (ethylene and
382 propylene), and benzene and toluene, which are important automotive exhaust tracers
383 (Song et al., 2021; Zhang et al., 2021b). Ethylene and propylene are important
384 components derived from vehicle-related activities. Previous studies of VOCs in
385 Zhengzhou have shown a high percentage of VOCs emitted from gasoline vehicles,
386 with the main source of alkanes being on-road mobile sources (Bai et al., 2020). The
387 daily variation of this source in Fig. S5 shows a bimodal trend, with peaks occurring in
388 the morning and evening peaks of traffic, consistent with motor vehicle emissions. Fig.
389 5d shows that this source is mainly from the west where wind speeds are below 2 m/s,
390 and in this direction, there are a number of urban arterial roads with high traffic volumes.
391 Therefore, factor 4 was defined as vehicular emission source.

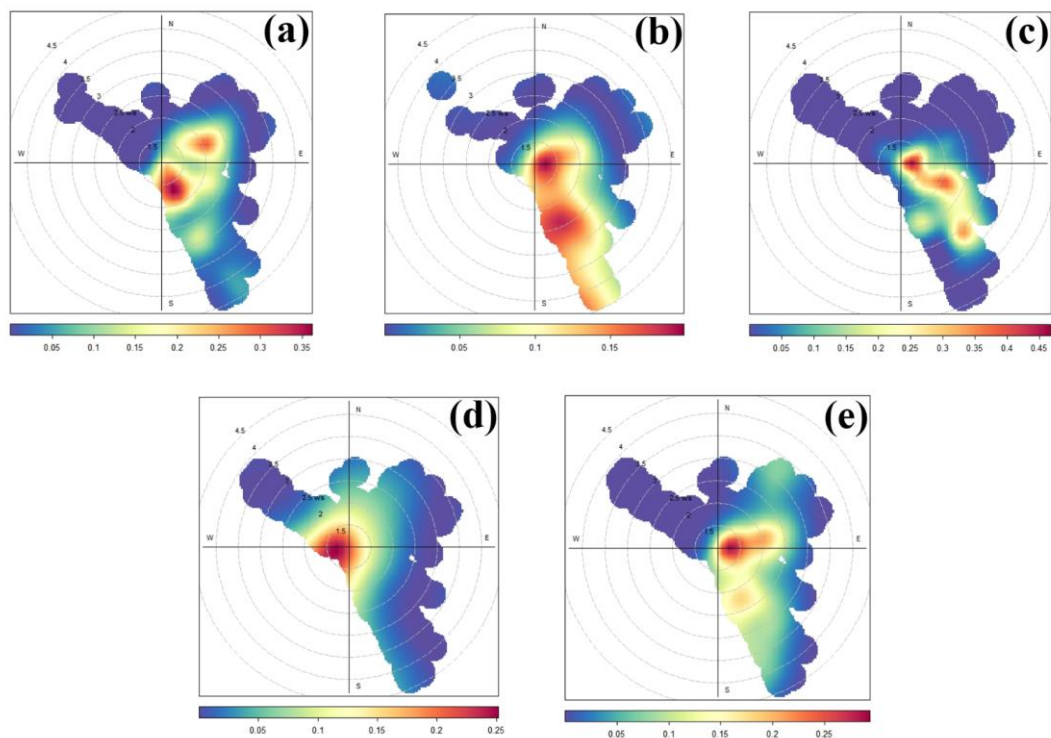
392 The highest contribution to factor 5 is chloromethane (62%). Benzene (46%) and
393 acetylene (41%) also contribute highly to factor 5. Chloromethane is the key tracer for
394 biomass combustion and acetylene is the key tracer for coal combustion (Xiong et al.,
395 2020). Therefore, factor 5 is defined as a combustion source. The CPF plot shows that
396 at wind speeds below 2 m/s, the north-east direction is the dominant source direction
397 (Fig. 5e).



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Fig. 4. Concentration of VOC species in each factor and contribution to each source.



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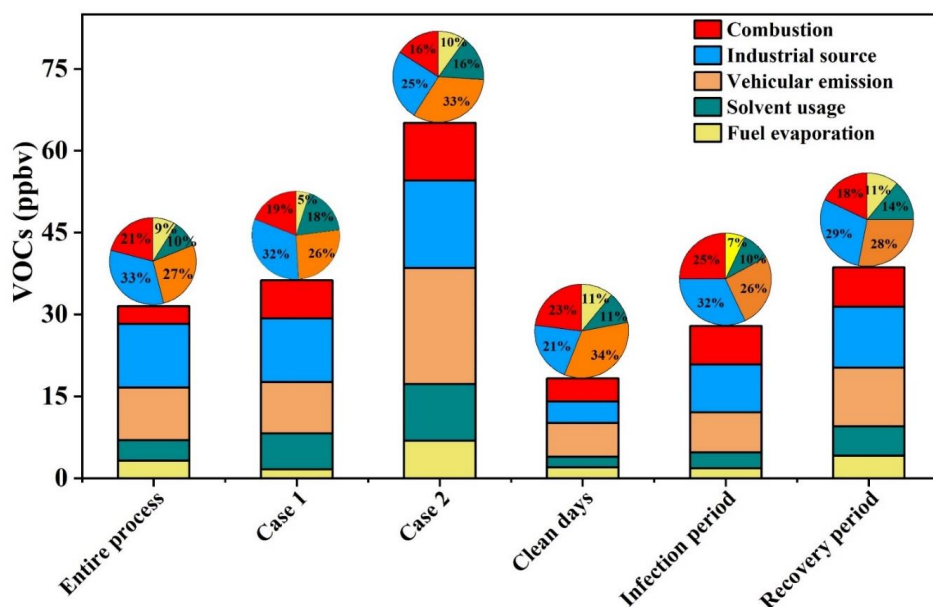
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Fig. 5. CPF plots of five VOCs sources obtained using the PMF model.

402 Note: a: Fuel evaporation; b: Solvent usage; c: Industrial source; d: Vehicular emission; e:
 403 Combustion.

404 Fig. S6 compares the differences in PMF source profiles between the Omicron
 405 infection period and the recovery period, as well as between the pollution day and the
 406 clean day. We present the concentrations of the five main VOCs in all five factors in
 407 Table S2. Ethane (vehicular emission), 2-methylpentane (fuel evaporation), benzene
 408 (industry source), chloromethane (combustion), and ethyl acetate (solvent usage) were
 409 selected as tracers for five sources. Ethane concentration in Case 2 (5.9 ppbv) is much
 410 higher than in other processes, and ethane concentration during the recovery period (3.4
 411 ppbv) is also higher than during the infection period (2.4 ppbv), which may to some
 412 extent reflect increased vehicular emissions during the recovery period.

413 Concentrations of most species were significantly higher during the recovery
 414 period than during the infection period. The representative pollution processes in both
 415 periods showed the same results as well, with a 79% higher concentration of TVOCs in
 416 Case 2 (65.1 ppbv) compared to Case 1 (36.3 ppbv) (Fig. 6). While in Case 1 industry
 417 was the dominant source of VOCs, by Case 2 motorized sources reached a
 418 concentration value of 21.2 ppbv, accounting for 33% of the observed VOCs, and
 419 became the dominant source of emissions. This is consistent with the fact that people's
 420 mobility activities have increased after the epidemic has entered the recovery period.
 421 As a group of VOCs species with the highest concentration share, ethane and propane
 422 contributed more to the clean days motor vehicle source than other processes, which
 423 also resulted in a 34% clean days motor vehicle source share.



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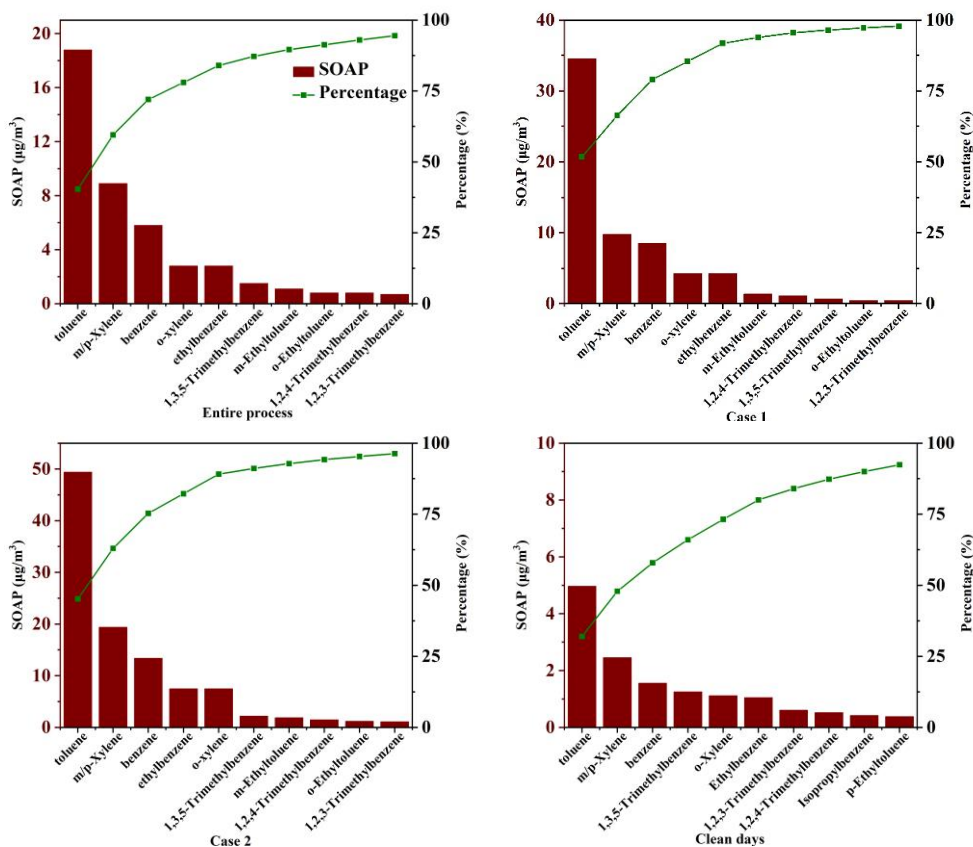
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Fig. 6. Contribution of each to VOCs for different processes.

426 3.3 SOAP

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

430 We have included quantitative analysis for SOAP as well. Fig. 7 shows the SOAP
431 concentrations and contribution rates of the top ten species throughout the entire
432 process, during two pollution processes, and clean days. The top ten species all reached
433 close to 100% of the total SOAP contribution, with Case 1 reaching 98%. In each
434 process, the composition of the top ten substances is essentially the same. Aromatic
435 hydrocarbons contributed the most, with BTEX always occupying the top five positions
436 and toluene the most. The SOAP values of the top ten contributing species for the two
437 polluting processes are shown in Tables S3 and S4. Toluene, the highest contributing
438 species, reached a SOAP value of 49.4 $\mu\text{g}/\text{m}^3$ in the most polluted Case 2, which was
439 3.2 times higher than the SOAP sum of all species on the clean day (15.5 $\mu\text{g}/\text{m}^3$). The
440 SOAP value for Case 1, which is also a contaminated process, was 67 $\mu\text{g}/\text{m}^3$, and the
441 main species (m/xylene: 9.8 $\mu\text{g}/\text{m}^3$, benzene: 8.5 $\mu\text{g}/\text{m}^3$) including toluene (34.6 $\mu\text{g}/\text{m}^3$)
442 were lower than those for Case 2 (m/xylene: 19.4 $\mu\text{g}/\text{m}^3$, benzene: 13.4 $\mu\text{g}/\text{m}^3$).



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Fig. 7. SOAP dominant species in different processes

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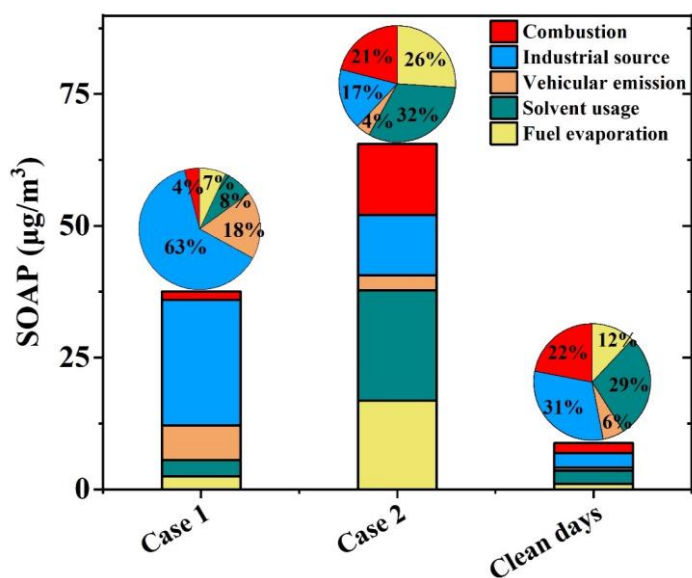
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Figure 8 shows the SOAP calculated after source resolution of the two pollution processes by PMF for clean days, respectively. In Case 1, industrial source is the dominant source with a contribution ratio of 63%. In Case 2, the pollution sources exhibit a more evenly distributed contribution, where the solvent usage and fuel evaporation sources emerge as the primary contributors to SOAP, with their respective contribution levels rising to 32% and 26%. Case 1 was during the infection period, when social activities had not yet returned to normal. In Case 2, when society had basically returned to normal, the increase in emissions from various sources resulted in a more balanced distribution of SOAP contributions and caused more severe PM_{2.5} pollution. In addition, a few days before Case 2, the Zhengzhou Municipal People's Government initiated the Heavy Pollution Weather Level II response (<https://sthjj.zhengzhou.gov.cn/tzgg/7037130.jhtml>) and introduced control measures for emissions from industrial and mobile sources, which resulted in a significant reduction of SOAP levels from industrial and motorized sources in Case 2. The clean day result with a SOAP of 8.8 $\mu\text{g}/\text{m}^3$ also indicates that industrial and solvent usage sources are the most dominant SOAP sources. The primary sources of aromatic compounds, which are the most significant contributors to SOAP, are solvent usage and industrial process emissions. This finding aligns with the results of other studies (Wu et al., 2017). Consequently, it is imperative to implement measures to reduce PM_{2.5} pollution by regulating emissions from industrial and solvent usage sources.



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Fig. 8. SOAP value and contribution ratio of each process

468 **4. Conclusions**

469 Continuous observation of VOCs during the infection of the Omicron epidemic
470 was carried out at an urban site in polluted Zhengzhou from December 1, 2022, to
471 January 31, 2023. The daily average concentration of PM_{2.5} ranged from 53.5 to 239.4
472 μg/m³ with an average value of 111.5 ± 45.1 μg/m³ during the whole period. The
473 concentration of TVOCs ranged from 15.6 to 57.1 ppbv with an average of 36.1 ± 21.0
474 ppbv, higher than the same period in last year (27.9 ± 12.7 ppbv, Lai et al., 2024). Two
475 representative contamination processes were identified (Case 1 during the infection
476 period and Case 2 during the recovery period). The concentration of TVOCs in Case 1
477 and Case 2 were 48.4 ± 20.4 and 67.6 ± 19.6 ppbv, respectively, increased by 63% and
478 188% compared with values during clean days. The average concentrations of PM_{2.5}
479 and TVOCs during Case 2 were 1.3 and 1.8 times of the values in Case 1. This is
480 consistent with the observed increase in pollutant emissions following the return to
481 normal social life from the period of Omicron infection. The highest volume
482 contributions of alkanes were found both in Case 1 (48%) and Case 2 (44%). Though
483 the volume contribution of aromatics were the lowest (6% in Case 1 and 7% in Case 2),
484 the highest increase ratio was found from clean days to polluted episodes. Low wind
485 speed and high humidity were the main meteorological reasons for the occurrence of
486 pollution. Analyzing the sources of VOCs revealed that VOCs were found to be affected
487 by a combination of local emissions and regional transport. The primary sources of
488 atmospheric VOCs in Zhengzhou were identified as industrial emissions (32%), vehicle
489 emissions (27%), and combustion (21%). Significant discrepancies were observed in
490 the sources of VOCs between the two pollution processes. In Case 1, industrial
491 emissions constituted the primary source of VOCs, accounting for 32% of the total
492 VOC concentration. In contrast, in Case 2, the proportion of vehicle emissions
493 increased to 33%, representing the primary source of VOCs.

494 A further analysis of the effect of VOCs on SOA generation reveals that aromatic
495 compounds are the primary contributors to SOAP, with BTEX being the predominant
496 contributor throughout the period. The SOAP values reached 37.6 and 65.6 μg/m³ in
497 Case 1 and Case 2, respectively. In Case 1, the greatest contribution to SOAP was made
498 by industrial sources (63%, 23.8 μg/m³), while vehicular sources, which constituted the
499 second most important source, accounted for only 18%. In Case 2, the contribution of
500 each VOC source was more evenly distributed, with solvent use sources and fuel

501 evaporation sources representing the primary contributors to SOAP, accounting for 32%
502 (20.9 $\mu\text{g}/\text{m}^3$) and 26% (16.8 $\mu\text{g}/\text{m}^3$), respectively. The SOAP result for the clean day
503 was 8.8 $\mu\text{g}/\text{m}^3$, with industrial sources and solvent use still being the primary
504 contributors. Therefore, the industrial and solvent use sectors are the predominant
505 sources of pollutants during this observation. The aforementioned results substantiate
506 the considerable impact of elevated emissions from all sources on the exacerbation of
507 pollution following the conclusion of the Omicron infection.

508 **Author contribution:**

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510 Dong Zhang: Data curation, Formal analysis, Review & Editing.

511 Zhe Dong: Data curation, Formal analysis, Review & Editing.

512 Xinshuai Song: Data curation, Formal analysis.

513 Ruiqin Zhang: Supervision, Writing-Review & Editing, Funding acquisition.

514 Xiao Li: Formal analysis, Investigation, Supervision, Writing-Review & Editing.

515 **Competing interests:**

516 The contact author has declared that none of the authors has any competing interests.

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