



1	The variations of VOCs based on the policy change of
2	Omicron in polluted winter in traffic-hub city, China
3	Bowen Zhang <sup>1, 3</sup> , Dong Zhang <sup>2, 3</sup> , Zhe Dong <sup>2, 3</sup> , Xinshuai Song <sup>1, 3</sup> , Ruiqin Zhang <sup>1, 3</sup> ,
4	Xiao Li <sup>1, 3,*</sup>
5	<sup>1</sup> School of Ecology and Environment, Zhengzhou University, Zhengzhou 450001,
6	China
7	<sup>2</sup> College of Chemistry, Zhengzhou University, Zhengzhou 450001, China
8	<sup>3</sup> Institute of Environmental Sciences, Zhengzhou University, Zhengzhou 450001,
9	China
10	Correspondence to: Xiao Li, E-mail address: lixiao9060@zzu.edu.cn
11	Abstract: Online volatile organic compounds (VOCs) were continuous
12	monitored before and after the Omicron policy change at an urban site in polluted
13	Zhengzhou from December 1, 2022, to January 31, 2023. The characteristics and
14	sources of VOCs were explored. The daily average concentration of $\text{PM}_{2.5}$ and total
15	VOCs (TVOCs) ranged from 54 to 239 $\mu g/m^3$ and from 15.6 to 57.1 ppbv with an
16	average value of 112 $\pm$ 45 $\mu g/m^3$ and 36.1 $\pm$ 21.0 ppbv, respectively during the entire
17	period. The values of $PM_{2.5}$ and TVOCs in Case 3 (pollution episode after the
18	abolishment of "Nucleic Acid Screening Measures for all staff" policy) were 1.3 and
19	1.8 times of the values in the Case 1 (pollution episode during "Nucleic Acid
20	Screening Measures for all staff" policy). The concentration of TVOCs in Case 1 and
21	Case 3 were 48.4 $\pm$ 20.4 and 67.6 $\pm$ 19.6 ppbv, respectively, increased by 63% and
22	188% compared with values during clean days. Alkanes were found to be the most
23	abundant compounds during the entire period. Equivalent volume contribution of
24	halogenated hydrocarbon and oxygenated VOCs (15%) were found the most in Case 3,
25	followed by alkenes (10%). Though the volume contributions of aromatics were the
26	lowest (6% in Case 1 and 7% in Case 3), the highest increasing ratio was found from
27	clean days to polluted episodes. Positive Matrix Factor model results showed that the
28	main source of VOCs during the observation period was industrial emissions, which
29	accounted for 30% of the TVOCs, followed by vehicular emission (24%) and
30	combustion (23%). The vehicular emission became the largest source during Case 1
31	(40%) and Case 3 (29%), consisting of large numbers of people going out after the
32	blockade. Secondary organic aerosol formation potential (SOAFP) values were 37
33	and 109 $\mu$ g/m <sup>3</sup> , respectively with the highest SOAFP contribution (17-19 $\mu$ g/m <sup>3</sup> and





- 34 31-51%) from vehicular emission both in Case 1 and Case 3. Solvent usage sources
- 35 had the second highest SOAFP value (9 and 16  $\mu$ g/m<sup>3</sup>) with the contributions of 23
- 36 and 31% in Case 1 and Case 3 respectively. The control of vehicular emission, and
- 37 solvent usage should be focused in Zhengzhou, and combustion was also important
- 38 for the control of PM<sub>2.5</sub> pollution in winter.
- 39
- 40 Keywords: Volatile organic compounds; Pollution episode; Source apportionment;





## 41 **1. Introduction**

42 Volatile organic compounds (VOCs) in the atmosphere have high reactivity and 43 can react with nitrogen oxides  $(NO_x)$  to form a series of secondary pollutants such as 44 ozone (O<sub>3</sub>) and secondary organic aerosol (SOA), resulting in regional air pollution 45 (Li et al., 2019; Hui et al., 2020). The problem of O<sub>3</sub> pollution has been plaguing major urban agglomerations in China (Zheng et al., 2010; Li et al., 2014; Wang et al., 46 47 2017). SOA is an important component of fine particulate matter ( $PM_{2,5}$ ) and 48 contributes significantly to haze pollution (Liu et al., 2019). PM<sub>2.5</sub> remains the most 49 significant air pollutant in many Chinese cities for years (Shao et al., 2016; Wu et al., 50 2016). In addition, VOCs, represented by the benzene homologues, can cause damage 51 to kidneys, liver, and nervous system of humans when they enter the body (Zhang et 52 al., 2018).

53 Studies have shown that the most common VOC components in China are 54 alkanes, olefins, aromatic hydrocarbons, oxygenated VOCs (OVOCs), and 55 halogenated hydrocarbons, among which alkanes are the most abundant species (Liu 56 et al., 2020; Zhang et al., 2021a). VOCs in the atmosphere have a wide range of 57 sources, and VOCs in different regions are affected by multiple factors such as local 58 geography, climate, and human activities (Mu et al., 2023; Zou et al., 2023). The 59 above reasons lead to significant regional and seasonal differences in the 60 characteristics of VOCs (Song et al., 2021). For example, the annual average 61 concentration of VOCs in the coastal background area of the Pearl River Delta is 9.3 62 ppbv. The seasonal variation trend of VOCs is high in autumn and winter and low in summer (Yun et al., 2021). In contrast, the average VOC concentration in autumn and 63 64 winter in Beijing was  $22.6 \pm 12.6$  ppbv, and the VOC concentration in the winter 65 heating period was twice that in the autumn non-heating period (Niu et al., 2022).

66 Moreover, the sources of VOC components in different regions are also related to 67 the local industrial structure and living habits. In rural areas of North China Plain in 68 winter, it is found that the SOA Formation Potential (SOAFP) of VOCs is 69 significantly higher under low NO<sub>x</sub> conditions than that under high NO<sub>x</sub> conditions, 70 and the increase of aromatic hydrocarbon emissions caused by coal combustion is the 71 main reason for the higher SOAFP in winter (Zhang et al., 2020). Li et al. (2022) 72 found that the average increased concentration of acetylene was 4.8 times from 73 autumn to winter in the Guanzhong Plain, indicating that fuel combustion during the





heating period in winter has a significant impact on the composition of VOCs. In contrast, continuous observations conducted by Zhou et al. (2022) in the suburbs of Dongguan in summer found that industrial solvent use, liquefied petroleum gas (LPG) and oil and gas volatilization were the main sources of VOCs. The results highlighted a wide variation of characteristics, sources and chemical reactions of VOCs in the atmosphere. Thus, it is necessary to investigate VOCs in different cities, especially when formulating control measures were carried out.

81 Zhengzhou, as the capital of Henan Province, is an important transportation hub 82 and economic center in the Central Plains region. Zhengzhou is currently facing 83 significant air pollution problems, with the Air Quality Index at the bottom of the 84 national ranking of 168 cities for many years. In January 2023, for example, the 85 number of polluted days with  $PM_{2.5}$  as the primary pollutant was 17 (55%), and the daily average value of PM<sub>2.5</sub> reached a maximum of 298  $\mu$ g/m<sup>3</sup>, which is almost 300% 86 higher than the Chinese daily average standard (grade II, 75  $\mu$ g/m<sup>3</sup>) (HC, 2022). The 87 88 studies of VOCs were carried out in Zhengzhou in recent years, which focused on the 89 characteristics and sources of VOCs during pollution episodes (Lai et al., 2024) or 90 before the coronavirus epidemic outbreak (Li et al., 2020; Zhang et al., 2021b).

91 In this study, a continuous online observation of VOCs in polluted winter at an 92 urban site was carried out, which covered the abolishment of lockdown measures in 93 Zhengzhou. A two-month-long lockdown measure was applied after the first Omicron 94 case of a student in Zhengzhou University was confirmed on October 8, 2022. 95 Lockdown measure was abolished at the beginning of December in 2022, which 96 resulted in a sharp increase of Omicron-infected people and a decrease in daily social 97 production activities. In fact, the "Nucleic Acid Screening Measures for all staff" 98 policy was also canceled on 8 December in 2022. People are basically homebound 99 after the lifting of the lockdown policy due to infection or fear of infection of 100 Omicron. The resumption of normal production and livelihoods was based on the 101 assumption of herd immunization. Therefore, the characteristics and variations of 102 VOCs during different periods were investigated to assess their impact on the 103 formation of SOA and to provide data support for future pollution control policies in 104 Zhengzhou.

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# 106 **2. Materials and methods**

## 107 **2.1 Sample collection and Chemical analysis**

108 The online VOCs observation station is located on the roof of the Zhengzhou 109 Environmental Protection Monitoring Center, which is in the urban area. The 110 sampling site is close to main roads on three sides (150 m away from Funiu Road on 111 the east side, 200 m away from Qinling Road on the west side, and connected to 112 Zhongyuan Road on the south side), and surrounded by residential areas and 113 commercial areas without other large nearby stationary sources. The sampling period 114 for this study was from December 1, 2022, to January 31, 2023, which is always the 115 most polluted period in the entire year. Apart from a brief occurrence of rain and snow 116 on December 25, the sampling days were either sunny or cloudy. The wind speed 117 (WS), temperature (Temp) and relative humidity (RH) during this period were 1.3  $\pm$ 0.9 m/s,  $5.3 \pm 3.2$  °C and  $38.9 \pm 19.0\%$  respectively, similar to the values observed in 118 119 previous years in Zhengzhou. It is interesting to point out that the sampling period in 120 the present study covered the entire infection period of Omicron in Zhengzhou, 121 including the phase of surge in infected population (Infection period, from 12/1 to 122 12/31 in 2022) and restoration of production and livelihood phase (Recovery period, 123 from 1/1 to 1/31 in 2023) (Fig. S1, CNCCP, 2023).

124 A total of 106 VOC species were monitored with the instrument of the TH-125 PKU300b of Wuhan Tianhong Company, which is an automatic continuous 126 monitoring system with a temporal resolution of 1 h. Detailed information of the 127 instrument was described by Zhang et al. (2021b). The monitored VOC species 128 include 29 alkanes, 11 olefins, 17 aromatic hydrocarbons, 35 halogenated 129 hydrocarbons, 12 OVOCs, 1 alkyne hydrocarbon (acetylene) and 1 sulfide (CS<sub>2</sub>). The 130 instrument was calibrated per week to ensure the accuracy of VOCs by injecting 131 standard gases with a five-point calibration curve. Refer to literature for the complete list of 106 VOCs (Huang et al., 2022). The detection limit of C2-C5 hydrocarbons 132 133 ranges from 0.007 to 0.051 ppbv, other hydrocarbons are 0.004-0.045 ppbv, 134 halogenated hydrocarbons 0.003-0.021 ppbv, OVOCs and other compounds of 0.005-135 0.015 ppbv.

Simultaneous observations at the same site were also carried out for particulate
matter (PM<sub>2.5</sub>, PM<sub>10</sub>), other trace gases (carbon monoxide (CO), O<sub>3</sub>, nitric oxide (NO),
nitrogen dioxide (NO<sub>2</sub>)), and meteorological data (Temp, RH, WS, and wind direction





139 (WD)) based on 1 h resolution.

## 140 2.2 Positive Matrix Factorization (PMF) model

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

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

147

where  $x_{ij}$  is the mass concentration of species *j* measured in sample *i*;  $g_{ik}$  is the contribution of factor *k* to the sample *i*;  $f_{kj}$  represents the content of the *j*th species in factor *k*;  $e_{ij}$  is the residual of species *j* in sample *i*; *p* represents the number of factors. The fitting objective of the PMF model is to minimize the function *Q* to obtain the factor contributions and contours. The formula for *Q* is given in Eq. (2):

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154 
$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^{2}$$
(2)

155

156 where n and m denote the number of samples and VOC species, respectively. 157 Concentrations and uncertainty data are required for the PMF model. In this study, the 158 median concentration of a given species is used to replace missing values with an 159 uncertainty of four times of the median values; data less than the Method Detection 160 Limit (MDL) were replaced with half the MDL, with an uncertainty of 5/6 of the 161 MDL; and the uncertainty for values greater than the MDL was calculated using Eq. 162 (3). In Eq. (3), *EF* is error fraction, expressed as the precision of VOCs species, and 163 the setting range can be adjusted from 5 to 20% according to the concentration 164 difference (Buzcu et al., 2006; Song et al., 2007); and  $c_{ij}$  is the concentration of species j in sample i: 165

166 
$$U_{ij} = \sqrt{\left(EF \times c_{ij}\right)^2 + (0.5 \times MDL)^2}$$
(3)





167 when the concentration of VOCs in the species is less than the value of the 168 detection limit  $U_{ij}$  is calculated using Eq. (4):

169 
$$U_{ij} = \left(\frac{5}{6}\right) MDL \tag{4}$$

170 VOC species and concentration input into PMF were carefully selected to ensure 171 the accuracy of the PMF results. Species were excluded when over 25% of the 172 samples were missing or concentrations values were below the MDL (Gao et al., 173 2018); VOCs with a short lifetime in the atmosphere were also excluded unless they 174 are source-relative species (Zhang et al., 2014; Shao et al., 2016). After that, retained 175 VOC species were categorized according to the signal-to-noise ratio (S/N) with S/N <176 0.2 species categorized as bad, 0.2 < S/N < 2 species categorized as weak; and S/N > 2177 2 species categorized as strong (Shao et al., 2016).

### 178 **2.3 SOA generation potential**

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

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183 
$$SOAFP_i = \frac{VOCs \ component \ i \ to \ SOA \ mass \ concentration \ increments}{Toluene \ to \ SOA \ mass \ concentration \ increment} \times 100$$
 (5)

184

SOAPF<sub>i</sub> for each VOC is taken from the literature (Derwent et al., 2010). The
SOAP was estimated by multiplying the SOAPF<sub>i</sub> value by the concentration of
individual VOC species. The SOAP calculations through each VOC are as follows:

189 
$$SOAP = \sum E_i \times SOAPF_i$$
 (6)

190 In eq. (6),  $E_i$  is the concentration of species *i*.

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## 192 **3. Results and discussion**

### 193 **3.1 Pollution characteristics**

Fig. 1 shows the time series of meteorological parameters, TVOCs, O<sub>3</sub>, NO<sub>x</sub>,
 SO<sub>2</sub>, CO and PM<sub>2.5</sub> during the observed periods. Low WS and Temp were found with





196 an average value of  $1.3 \pm 0.6$  m/s and  $5.0 \pm 2.5$  °C, respectively, during the entire 197 period, comparable with the contemporaneous results at the same site in 2021 (Lai et 198 al., 2024). The average value of RH was  $38.9 \pm 16.7\%$ . A total of 62 days of valid data 199 was acquired with the daily average concentration of PM<sub>2.5</sub> ranging from 54 to 239 200 µg/m<sup>3</sup>, with the average value of  $112 \pm 45 \mu$ g/m<sup>3</sup>. The concentration of TVOCs 201 ranged from 15.6 to 57.1 ppbv with an average of  $36.1 \pm 21.0$  ppbv, higher than the 202 same period in last year (27.9 ± 12.7 ppbv, Lai et al., 2024).

203 The comparisons of average concentrations between different periods are presented in Tables 1 and 2. WS, Temp and RH conditions during infection and 204 205 recovery periods were generally similar. However, the average concentration of PM<sub>2.5</sub> during the recovery period was 1.6 times of the value during the infection period. 206 207 Furthermore, the concentrations of other pollutants including  $SO_2$ ,  $NO_2$ , CO, and  $O_3$ 208 all showed a similar trend between infection and recovery periods. The TVOC 209 concentration during the recovery period was 1.2 times of the value during the 210 infection period, showing an obvious increase trend after resuming production. 211 Decreased trends of air pollutants were found in other studies before and after the 212 outbreak of the novel coronavirus (COVID-19) in early 2020 (Qi et al., 2021; Wang et 213 al., 2021).



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215 216

Fig. 1 Time series of WS, WD, T, RH, CO,  $PM_{2.5}$ , NO, TVOCs,  $NO_x$  and  $O_3$  during the observation period.





217 A total of five pollution episodes were identified based on the daily average 218 concentration of PM<sub>2.5</sub> being above 75 µg/m<sup>3</sup> (Grade II limit value in China) for at 219 least three days, including two pollution processes during infection periods (Case 1 220 and Case 2 in December) and three pollution processes during recovery periods (Case 221 3, Case 4 and Case 5 in January). Apart from that, clean days were identified as PM<sub>2.5</sub> 222 being below 35 µg/m<sup>3</sup> (Grade I limit value in China). Among them, Case 1 (from 223 December 5 to December 10 and Case 3 (from January 1 to January 8) were selected 224 as representative pollution processes because of the long duration and high level of 225 contamination.



Fig. 2 The concentration of  $PM_{2.5}$ ,  $NO_x$ , TVOCs and the composition ratio of VOCs in Case 1 and Case 3. As for the two representative pollution processes (Case 1 during the infection period and Case 3 during the recovery period), the concentration of TVOCs in Case 1 and Case 3 were  $48.4 \pm 20.4$  and  $67.6 \pm 19.6$  ppbv (Fig. 2), respectively, increased by 63% and 188% compared with values during clean days. The average concentrations of PM<sub>2.5</sub> and TVOCs during Case 3 were 1.3 and 1.8 times the values in Case 1. The





234	highest volume contributions of alkanes were found both in Case 1 (48%) and Case 3
235	(44%), consistent with the results in the Yangtze River Delta region (36-43%, Liu et
236	al., 2023). While alkenes exhibited higher volume percentages of 13% in Case 1,
237	followed by halogenated hydrocarbon (12%) and OVOCs (10%). Higher volume
238	percentages of alkanes and alkenes in Case 1 were similar to the results in the
239	gasoline evaporation site in winter (Niu et al., 2022). Equivalent volume contribution
240	of halogenated hydrocarbon and OVOCs (15%) were found in Case 3, followed by
241	alkenes (10%). Though the volume contributions of aromatics were the lowest (6% in
242	Case 1 and 7% in Case 3), the highest increase ratio was found from clean days to
243	polluted episodes.

Table 1 The average concentrations of meteorological parameters and pollutants during differentprocesses.

Catagory	Entire process	Infection period	Recovery period	Case 1	Case 3
Category	N = 62  days	N = 31 days	N = 31 days	N = 6 days	N = 8 days
WS (m/s)	$1.3 \pm 0.6$	$1.4 \pm 0.6$	$1.3 \pm 0.6$	$1.2\pm0.9$	$0.9\pm0.7$
Temp (°C)	$5.0\pm2.5$	$4.7\pm1.7$	$5.4\pm3.1$	$6.1\pm2.2$	$7.4\pm3.5$
RH (%)	$38.9 \pm 16.7$	$37.6 \pm 15.5$	$40.2\pm18.2$	$55.7 \pm 14.7$	$42.0\pm12.1$
TVOCs (ppbv)	$36.1\pm21.0$	$31.9 \pm 18.1$	$39.8\pm22.4$	$37.6\pm27.0$	$68.2 \pm 19.6$
$SO_2 (\mu g/m^3)$	$11.4\pm2.7$	$10.2\pm2.8$	$12.7\pm2.3$	$11.0\pm3.7$	$16.2\pm6.1$
$NO_2(\mu g/m^3)$	$47.2\pm10.0$	$46.8\pm8.6$	$47.8 \pm 11.7$	$62.7\pm20.5$	$65.0\pm21.3$
CO (mg/m <sup>3</sup> )	$0.9\pm0.2$	$0.8\pm0.2$	$1.1\pm0.2$	$1.2\pm0.5$	$1.3\pm0.4$
$O_3(\mu g/m^3)$	$34.9\pm6.0$	$31.1\pm4.5$	$39.0\pm4.6$	$21.8\pm23.7$	$32.5\pm29.6$
$PM_{2.5} (\mu g/m^3)$	$112\pm45$	$87\pm35$	$138\pm40$	$143\pm67$	$182\pm83$

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

Category	Entire process	Infection period	Recovery period	Case 1	Case 3	Clean days
TVOCs	$36.1\pm21.0$	$31.9 \pm 18.1$	$39.8\pm22.4$	$48.4\pm20.4$	$67.6 \pm 19.6$	$17.5\pm9.5$
alkanes	$16.8\pm9.2$	$15.0\pm8.4$	$18.4\pm9.5$	$23.1\pm10.0$	$29.5\pm8.4$	$9.2\pm5.6$
alkenes	$4.1\pm2.7$	$3.8\pm2.6$	$4.4\pm2.7$	$6.5\pm2.9$	$7.0\pm2.6$	$1.7 \pm 1.3$
alkynes	$3.1\pm2.0$	$2.7\pm1.7$	$3.4 \pm 2.1$	$4.3\pm2.0$	$5.8 \pm 1.9$	$1.3\pm0.8$
aromatics	$2.1\pm2.0$	$1.8 \pm 1.5$	$2.3\pm2.2$	$3.0\pm1.8$	$4.9\pm2.8$	$0.7\pm0.5$
halogenated hydrocarbon	$5.4\pm3.3$	$4.4\pm2.3$	$6.2\pm3.8$	$6.0\pm1.9$	$10.7\pm3.6$	$2.7\pm1.4$
OVOCs	$4.6\pm3.2$	$3.5\pm2.7$	$5.1\pm3.5$	$5.0\pm2.4$	$9.7\pm2.8$	$1.9\pm1.1$





# 247 **3.2 Source appointment**

248	Specific VOC ratios can be used for initial source identification of VOCs and
249	determination of photochemical ages of air masses (Monod et al., 2001; An et al.,
250	2014; Li et al., 2019). In this study, the ratios of toluene/benzene (T/B), isopentane/n-
251	pentane, isobutane/n-butane, and m/p-xylene/ethylbenzene (X/E) were selected to
252	initially identify the potential sources of VOCs (Fig. 3).
253	Generally, T/B $\leq$ 2.2 indicates that VOCs are mainly influenced by transportation

254 emissions (Wang et al., 2013; Yao et al., 2015), T/B > 8.8 indicates VOCs are mainly 255 influenced by solvent use (Song et al., 2021), while other values indicates that VOCs 256 are influenced by multiple emissions (Mo et al., 2015; Shi et al., 2015). The average 257 T/B value was  $1.0 \pm 0.6$  during the whole period, indicating the significant influence 258 of transportation emissions in this study. In addition, isopentane/n-pentane 259 concentration ratios of 0.6-0.8, 0.8-0.9, 2.2-3.8, and 1.8-4.6 for coal combustion, 260 natural gas emissions, vehicle emissions, and fuel evaporation, respectively (Liu et al., 261 2008; Li et al., 2019). Isobutane/n-butane concentration ratios of 0.2-0.3, 0.4-0.6, and ratios of 0.6-1.0 represent vehicle emissions, LPG use, and natural gas emissions, 262 263 respectively (Russo et al., 2010; Zheng et al., 2018). The ratios of isopentane/n-264 pentane and isobutane/n-butane in this study were 1.33 and 0.50, respectively, 265 suggesting that the concentration of VOCs were also influenced by fuel evaporation, 266 natural gas emissions, and LPG use (Shao et al., 2016; Zeng et al., 2023).

The ratio of X/E can be used to infer the photochemical age of the air mass. X/E ratios around 2.5-2.9 are typical of urban areas, indicating that VOCs are mainly from the urban area (fresh air mass) (Kumar et al., 2018). When this ratio is significantly lower than 3, it indicates that VOCs are mainly transported from distant sources (aging air masses) (Kumar et al., 2018). The average X/E value in this study was 2.0 (Fig. 3(d)), indicating that the measured air VOC content was influenced by both remote sources and urban area emissions.







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#### Fig. 3 Correlation analysis between specific VOC species

276 Figure 4 shows the chemical profiles of individual VOCs resolved by the PMF 277 model during the entire observation period. After examining 3-6 factors, 20 base runs 278 with 5 factors were eventually selected to represent the final result in four cases (Fig. 279 S1). These five factors eventually selected as potential sources for the observed VOCs 280 are: (1) Fuel evaporation; (2) Solvent usage; (3) Vehicular emission; (4) Industrial 281 source; and (5) Combustion. These 5 factors have been commonly reported before, 282 e.g., in Shijiazhuang, northern China (Guan et al, 2023) and in Beijing (Cui et al., 283 2022).

Alkanes of C4-C6 substances were predominant in factor 1, including 2methylpentane, 3-methylpentane, isobutane, n-butane, isopentane and n-pentane from oil and gas (Xiong et al., 2020). Among them, isopentane and n-pentane are typical tracers of volatile gasoline. Therefore, factor 1 was identified as the source of oil and gas volatilization.

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 chloride is often used as a chemical solvent, while esters are mostly





used as industrial solvents or adhesives (Li et al., 2015). Factor 2 is determined to be asolvent usage source.

295 Factor 3 is characterized by relatively high levels of C2-C6 low-carbon alkanes 296 (ethane, propane, isopentane, n-pentane, isobutane and n-butane), olefins (ethylene 297 and propylene), and benzene and toluene, which are important automotive exhaust tracers (Song et al., 2021; Zhang et al., 2021b). Ethylene and propylene are important 298 299 components derived from vehicle-related activities. The contribution of methyl tertbutyl ether to this factor is also relatively high, and methyl tert-butyl ether is often 300 301 used as an oil and gas additive. Previous studies of VOCs in Zhengzhou have shown a high percentage of VOCs emitted from gasoline vehicles, with the main source of 302 303 alkanes being on-road mobile sources (Bai et al., 2020). Therefore, factor 3 was 304 defined as vehicular emission source.

There are rubber and plastic products industries distributed around the area where the sampling point is located. factor 4 is dominated by C3-C8 alkanes, olefins and alkynes, with relatively high concentrations of chloromethane and other substances. The above substances are commonly emitted from industrial processes (Shao et al., 2016), so Factor 4 is defined as an industrial source.

The highest contributor to factor 5 was chloromethane (68%), with similarly high contributions from benzene (42%) and acetylene (38%), chloromethane being a key tracer for biomass combustion, and acetylene being a key tracer for coal combustion (Xiong et al., 2020). Therefore, factor 5 is defined as a combustion source.









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

316 The results of source analysis of the whole stage, two pollution processes and 317 clean days are shown in Fig. 5. The main source of VOCs during the observation period was industrial emissions, which accounted for 30% of the TVOCs, followed by 318 319 vehicular emission (24%) and combustion (23%). There were significant differences 320 in the sources of VOCs for different pollution processes. The vehicular emission 321 became the largest source during Case 1 (40%) and Case 3 (29%), consisting with 322 large numbers of people going out after the blockade. Meanwhile, the contribution of 323 industrial source decreased from 30% during the entire process to 23-25% during Case 1 and Case 3. Fuel evaporation and the solvent use sources accounted for a 324 325 comparable value during all stages with a total value from 22% to 29%.







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Fig. 5 Contribution of each source to VOCs for different processes

328 3.3 SOAFP

329 SOA has a significant impact on PM<sub>2.5</sub> pollution (Liu et al., 2021). The SOAFP 330 were calculated during Case 1 and Case 3 (Table S1-S2 and Fig. 6). The categories of species contributing to SOAFP were similar in the different processes, with large 331 332 differences in concentrations. The top 10 VOCs contributed more than 95% to SOAFP 333 generation, and the contribution of aromatic hydrocarbons was dominant with BTEX 334 consistently occupying the top five positions and the largest contributor of toluene. 335 The main sources of aromatic compounds are solvent use and industrial process 336 emissions, similar to the result in other study (Wu et al., 2017). SOAFP values were 337 37 and 109 µg/m<sup>3</sup>, respectively in Case 1 and Case 3. Among them, vehicular 338 emission source had the highest SOAFP values (19 and 17  $\mu$ g/m<sup>3</sup>) and contributed 51% 339 and 31%, in Case 1 and Case 3, respectively. Solvent usage source had the second highest SOAFP values (9 and 16  $\mu$ g/m<sup>3</sup>) with the contributions of 23% and 31%. 340 341 Apart from that, combustion source in Case 3 (17  $\mu$ g/m<sup>3</sup>) was also abundant with a 342 contribution of 31%. The contributions of industrial source (3.7 and 3.4  $\mu$ g/m<sup>3</sup>) and 343 fuel evaporation (2.3 and 1.0  $\mu$ g/m<sup>3</sup>) were relatively low with values between 6-10% and 2-6% respectively. Therefore, the focus should be on the control of vehicular 344





- 345 emission, solvent usage as well as combustion for the control of PM<sub>2.5</sub> pollution in
- 346 winter.



347 348 349

### Fig. 6. SOAFP value and contribution ratio of each component

### 350 4. Conclusions

351 Continuous observation of VOCs during the infection of the Omicron epidemic 352 was carried out at an urban site in a polluted traffic-hub city Zhengzhou in central China from December 1, 2022, to January 31, 2023. The daily average concentration 353 354 of PM<sub>2.5</sub> ranged from 54 to 239  $\mu$ g/m<sup>3</sup> with an average value of 112 ± 45  $\mu$ g/m<sup>3</sup> during the whole period. The daily average concentration of PM2.5 during the 355 356 sampling period is 0.7-3.2 times of the Grade II limit value in China, over 70% days 357 exceeding 75 µg/m<sup>3</sup>. The concentration of TVOCs ranged from 15.6 to 57.1 ppbv 358 with an average of  $36.1 \pm 21.0$  ppbv.

The values of PM<sub>2.5</sub> and TVOCs in Case 3 (pollution episode after the abolishment of "Nucleic Acid Screening Measures for all staff" policy) were 1.3 and 1.8 times of the values in the Case 1 (pollution episode during "Nucleic Acid Screening Measures for all staff" policy).

A total of five pollution episodes were identified including two representative pollution processes (Case 1 during "Nucleic Acid Screening Measures for all staff"





policy and Case 3 after the abolishment of "Nucleic Acid Screening Measures for all 365 staff" policy). The concentration of TVOCs in Case 1 and Case 3 were  $48.4 \pm 20.4$ 366 367 and  $67.6 \pm 19.6$  ppby, respectively, increased by 63% and 188% compared with values 368 during clean days. The average concentrations of  $PM_{2.5}$  and TVOCs during Case 3 369 were 1.3 and 1.8 times of the values in Case 1. The highest volume contributions of 370 alkanes were found both in Case 1 (48%) and Case 3 (44%). Though the volume 371 contribution of aromatics were the lowest (6% in Case 1 and 7% in Case 3), the highest increase ratio was found from clean days to polluted episodes. Aromatic 372 373 compounds are the main contributors to SOAFP, with BTEX being the main 374 contributor during the entire period. SOAFP values reached 37 and 109  $\mu$ g/m<sup>3</sup>, 375 respectively in Case 1 and Case 3.

376 Preliminary identification of local sources of contamination through T/B, 377 isopentane/n-pentane, isobutane/n-butane, and X/E ratios. The average X/E value was 2.0, indicating that the measured air VOCs levels were influenced by both remote 378 379 sources and urban area emissions. Five major pollution sources were obtained by the 380 PMF receptor model, including industrial emissions (30%), vehicular emission (24%), combustion (23%), fuel evaporation (12%) and solvent use source (11%). There were 381 382 significant differences in the sources of VOCs in different pollution periods. Vehicular emission source became the largest source during Case 1 (40%) and Case 3 (29%) and 383 384 the contribution of industrial source decreased from 30% during the entire process to 385 23-25% during Case 1 and Case 3. Vehicular emission also had the highest SOAFP 386 value (19 and 17  $\mu$ g/m<sup>3</sup>) followed by solvent usage (9 and 16  $\mu$ g/m<sup>3</sup>). Apart from that, 387 combustion sources in Case 3 (17 µg/m<sup>3</sup>) was also abundant with a contribution of 388 31%. The focus should be on the control of vehicular emission, solvent usage as well 389 as combustion for the control of PM2.5 pollution in winter.

#### **390** Author contribution:

- 391 Bowen Zhang: Data curation, Methodology, Formal analysis, Writing Original Draft.
- 392 Dong Zhang: Data curation, Formal analysis, Review & Editing.
- 393 Zhe Dong: Data curation, Formal analysis, Review & Editing.
- 394 Xinshuai Song: Data curation, Formal analysis.
- 395 Ruiqin Zhang: Supervision, Writing-Review & Editing, Funding acquisition.
- 396 Xiao Li: Formal analysis, Investigation, Supervision, Writing-Review & Editing.





### 397 Competing interests:

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

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