The variations of VOCs based on the policy change of Omicron in polluted winter in traffic-hub city, China

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Abstract: Online volatile organic compounds (VOCs) were continuous 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 explored. The daily average concentration of PM₂.₅ and total VOCs (TVOCs) ranged from 54 to 239 µg/m³ and from 15.6 to 57.1 ppbv with an average value of 112 ± 45 µg/m³ and 36.1 ± 21.0 ppbv, respectively during the entire period. The values of PM₂.₅ 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). The concentration of TVOCs in Case 1 and Case 3 were 48.4 ± 20.4 and 67.6 ± 19.6 ppbv, respectively, increased by 63% and 188% compared with values during clean days. Alkanes were found to be the most abundant compounds during the entire period. Equivalent volume contribution of halogenated hydrocarbon and oxygenated VOCs (15%) were found the most in Case 3, followed by alkenes (10%). Though the volume contributions of aromatics were the lowest (6% in Case 1 and 7% in Case 3), the highest increasing ratio was found from clean days to polluted episodes. Positive Matrix Factor model results showed that the main source of VOCs during the observation period was industrial emissions, which accounted for 30% of the TVOCs, followed by vehicular emission (24%) and combustion (23%). The vehicular emission became the largest source during Case 1 (40%) and Case 3 (29%), consisting of large numbers of people going out after the blockade. Secondary organic aerosol formation potential (SOAFP) values were 37 and 109 µg/m³, respectively with the highest SOAFP contribution (17-19 µg/m³ and

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31-51%) from vehicular emission both in Case 1 and Case 3. Solvent usage sources had the second highest SOAFP value (9 and 16 μg/m³) with the contributions of 23 and 31% in Case 1 and Case 3 respectively. The control of vehicular emission, and solvent usage should be focused in Zhengzhou, and combustion was also important for the control of PM$_{2.5}$ pollution in winter.

Keywords: Volatile organic compounds; Pollution episode; Source apportionment;
1. Introduction

Volatile organic compounds (VOCs) in the atmosphere have high reactivity and can react with nitrogen oxides (NOx) to form a series of secondary pollutants such as ozone (O3) and secondary organic aerosol (SOA), resulting in regional air pollution (Li et al., 2019; Hui et al., 2020). The problem of O3 pollution has been plaguing major urban agglomerations in China (Zheng et al., 2010; Li et al., 2014; Wang et al., 2017). SOA is an important component of fine particulate matter (PM2.5) and contributes significantly to haze pollution (Liu et al., 2019). PM2.5 remains the most significant air pollutant in many Chinese cities for years (Shao et al., 2016; Wu et al., 2016). In addition, VOCs, represented by the benzene homologues, can cause damage to kidneys, liver, and nervous system of humans when they enter the body (Zhang et al., 2018).

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

Moreover, the sources of VOC components in different regions are also related to the local industrial structure and living habits. In rural areas of North China Plain in winter, it is found that the SOA Formation Potential (SOAFP) of VOCs is significantly higher under low NOx conditions than that under high NOx conditions, and the increase of aromatic hydrocarbon emissions caused by coal combustion is the main reason for the higher SOAFP in winter (Zhang et al., 2020). Li et al. (2022) found that the average increased concentration of acetylene was 4.8 times from 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.

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

In this study, a continuous online observation of VOCs in polluted winter at an urban site was carried out, which covered the abolishment of lockdown measures in Zhengzhou. A two-month-long lockdown measure was applied after the first Omicron case of a student in Zhengzhou University was confirmed on October 8, 2022. Lockdown measure was abolished at 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 8 December in 2022. People are basically homebound after the lifting of the lockdown policy due to infection or fear of infection of Omicron. The resumption of normal production and livelihoods was based on the assumption of herd immunization. Therefore, the characteristics and variations of VOCs during different periods were investigated to assess their impact on the formation of SOA and to provide data support for future pollution control policies in Zhengzhou.
2. Materials and methods

2.1 Sample collection and Chemical analysis

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

A total of 106 VOC species were monitored with the instrument of the TH-PKU300b of Wuhan Tianhong Company, which is an automatic continuous monitoring system with a temporal resolution of 1 h. Detailed information of the instrument was described by Zhang et al. (2021b). The monitored VOC species include 29 alkanes, 11 olefins, 17 aromatic hydrocarbons, 35 halogenated hydrocarbons, 12 OVOCs, 1 alkyne hydrocarbon (acetylene) and 1 sulfide (CS₂). The instrument was calibrated per week to ensure the accuracy of VOCs by injecting 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 ranges from 0.007 to 0.051 ppbv, other hydrocarbons are 0.004–0.045 ppbv, halogenated hydrocarbons 0.003-0.021 ppbv, OVOCs and other compounds of 0.005–0.015 ppbv.

Simultaneous observations at the same site were also carried out for particulate matter (PM₂.₅, PM₁₀), other trace gases (carbon monoxide (CO), O₃, nitric oxide (NO), nitrogen dioxide (NO₂)), and meteorological data (Temp, RH, WS, and wind direction).
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):

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}
\]

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):

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

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

\[
u_{ij} = \sqrt{(EF \times c_{ij})^2 + (0.5 \times MDL)^2}
\]
when the concentration of VOCs in the species is less than the value of the detection limit $U_{ij}$ is calculated using Eq. (4):

$$U_{ij} = \left(\frac{5}{6}\right) MDL$$  \hspace{1cm} (4)

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

### 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:

$$SOAFP_i = \frac{VOCs \ component \ i \ to \ SOA \ mass \ concentration \ increments}{Toluene \ to \ SOA \ mass \ concentration \ increment} \times 100$$  \hspace{1cm} (5)

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

$$SOAP = \sum E_i \times SOAP_i$$  \hspace{1cm} (6)

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

### 3. Results and discussion

#### 3.1 Pollution characteristics

Fig. 1 shows the time series of meteorological parameters, TVOCs, $O_3$, $NO_x$, $SO_2$, CO and PM$_{2.5}$ during the observed periods. Low WS and Temp were found with...
an average value of 1.3 ± 0.6 m/s and 5.0 ± 2.5 °C, respectively, during the entire period, comparable with the contemporaneous results at the same site in 2021 (Lai et al., 2024). The average value of RH was 38.9 ± 16.7%. A total of 62 days of valid data was acquired with the daily average concentration of PM$_{2.5}$ ranging from 54 to 239 µg/m$^3$, with the average value of 112 ± 45 µg/m$^3$. The concentration of TVOCs ranged from 15.6 to 57.1 ppbv with an average of 36.1 ± 21.0 ppbv, higher than the same period in last year (27.9 ± 12.7 ppbv, Lai et al., 2024).

The comparisons of average concentrations between different periods are presented in Tables 1 and 2. WS, Temp and RH conditions during infection and recovery periods were generally similar. However, the average concentration of PM$_{2.5}$ during the recovery period was 1.6 times of the value during the infection period. Furthermore, the concentrations of other pollutants including SO$_2$, NO$_2$, CO, and O$_3$ all showed a similar trend between infection and recovery periods. The TVOC concentration during the recovery period was 1.2 times of the value during the infection period, showing an obvious increase trend after resuming production. Decreased trends of air pollutants were found in other studies before and after the outbreak of the novel coronavirus (COVID-19) in early 2020 (Qi et al., 2021; Wang et al., 2021).

Fig. 1 Time series of WS, WD, T, RH, CO, PM$_{2.5}$, NO, TVOCs, NO$_x$, and O$_3$ during the observation period.
A total of five pollution episodes were identified based on the daily average concentration of PM$_{2.5}$ being above 75 µg/m$^3$ (Grade II limit value in China) for at least three days, including two pollution processes during infection periods (Case 1 and Case 2 in December) and three pollution processes during recovery periods (Case 3, Case 4 and Case 5 in January). Apart from that, clean days were identified as PM$_{2.5}$ being below 35 µg/m$^3$ (Grade I limit value in China). Among them, Case 1 (from December 5 to December 10) and Case 3 (from January 1 to January 8) were selected as representative pollution processes because of the long duration and high level of contamination.

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 ± 20.4 and 67.6 ± 19.6 ppbv (Fig. 2), respectively, increased by 63% and 188% compared with values during clean days. The average concentrations of PM$_{2.5}$ and TVOCs during Case 3 were 1.3 and 1.8 times the values in Case 1. The
highest volume contributions of alkanes were found both in Case 1 (48%) and Case 3 (44%), consistent with the results in the Yangtze River Delta region (36-43%, Liu et al., 2023). While alkenes exhibited higher volume percentages of 13% in Case 1, followed by halogenated hydrocarbon (12%) and OVOCs (10%). Higher volume percentages of alkanes and alkenes in Case 1 were similar to the results in the gasoline evaporation site in winter (Niu et al., 2022). Equivalent volume contribution of halogenated hydrocarbon and OVOCs (15%) were found in Case 3, followed by alkenes (10%). Though the volume contributions 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.

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

<table>
<thead>
<tr>
<th>Category</th>
<th>Entire process</th>
<th>Infection period</th>
<th>Recovery period</th>
<th>Case 1</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N = 62 days</td>
<td>N = 31 days</td>
<td>N = 31 days</td>
<td>N = 6 days</td>
<td>N = 8 days</td>
</tr>
<tr>
<td>WS (m/s)</td>
<td>1.3 ± 0.6</td>
<td>1.4 ± 0.6</td>
<td>1.3 ± 0.6</td>
<td>1.2 ± 0.9</td>
<td>0.9 ± 0.7</td>
</tr>
<tr>
<td>Temp (℃)</td>
<td>5.0 ± 2.5</td>
<td>4.7 ± 1.7</td>
<td>5.4 ± 3.1</td>
<td>6.1 ± 2.2</td>
<td>7.4 ± 3.5</td>
</tr>
<tr>
<td>RH (%)</td>
<td>38.9 ± 16.7</td>
<td>37.6 ± 15.5</td>
<td>40.2 ± 18.2</td>
<td>55.7 ± 14.7</td>
<td>42.0 ± 12.1</td>
</tr>
<tr>
<td>TVOCs (ppbv)</td>
<td>36.1 ± 21.0</td>
<td>31.9 ± 18.1</td>
<td>39.8 ± 22.4</td>
<td>37.6 ± 27.0</td>
<td>68.2 ± 19.6</td>
</tr>
<tr>
<td>SO₂ (µg/m³)</td>
<td>11.4 ± 2.7</td>
<td>10.2 ± 2.8</td>
<td>12.7 ± 2.3</td>
<td>11.0 ± 3.7</td>
<td>16.2 ± 6.1</td>
</tr>
<tr>
<td>NO₂ (µg/m³)</td>
<td>47.2 ± 10.0</td>
<td>46.8 ± 8.6</td>
<td>47.8 ± 11.7</td>
<td>62.7 ± 20.5</td>
<td>65.0 ± 21.3</td>
</tr>
<tr>
<td>CO (mg/m³)</td>
<td>0.9 ± 0.2</td>
<td>0.8 ± 0.2</td>
<td>1.1 ± 0.2</td>
<td>1.2 ± 0.5</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>O₃ (µg/m³)</td>
<td>34.9 ± 6.0</td>
<td>31.1 ± 4.5</td>
<td>39.0 ± 4.6</td>
<td>21.8 ± 23.7</td>
<td>32.5 ± 29.6</td>
</tr>
<tr>
<td>PM₂.₅ (µg/m³)</td>
<td>112 ± 45</td>
<td>87 ± 35</td>
<td>138 ± 40</td>
<td>143 ± 67</td>
<td>182 ± 83</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Category</th>
<th>Entire process</th>
<th>Infection period</th>
<th>Recovery period</th>
<th>Case 1</th>
<th>Case 3</th>
<th>Clean days</th>
</tr>
</thead>
<tbody>
<tr>
<td>TVOCs</td>
<td>36.1 ± 21.0</td>
<td>31.9 ± 18.1</td>
<td>39.8 ± 22.4</td>
<td>48.4 ± 20.4</td>
<td>67.6 ± 19.6</td>
<td>17.5 ± 9.5</td>
</tr>
<tr>
<td>alkanes</td>
<td>16.8 ± 9.2</td>
<td>15.0 ± 8.4</td>
<td>18.4 ± 9.5</td>
<td>23.1 ± 10.0</td>
<td>29.5 ± 8.4</td>
<td>9.2 ± 5.6</td>
</tr>
<tr>
<td>alkenes</td>
<td>4.1 ± 2.7</td>
<td>3.8 ± 2.6</td>
<td>4.4 ± 2.7</td>
<td>6.5 ± 2.9</td>
<td>7.0 ± 2.6</td>
<td>1.7 ± 1.3</td>
</tr>
<tr>
<td>alkynes</td>
<td>3.1 ± 2.0</td>
<td>2.7 ± 1.7</td>
<td>3.4 ± 2.1</td>
<td>4.3 ± 2.0</td>
<td>5.8 ± 1.9</td>
<td>1.3 ± 0.8</td>
</tr>
<tr>
<td>aromatics</td>
<td>2.1 ± 2.0</td>
<td>1.8 ± 1.5</td>
<td>2.3 ± 2.2</td>
<td>3.0 ± 1.8</td>
<td>4.9 ± 2.8</td>
<td>0.7 ± 0.5</td>
</tr>
<tr>
<td>halogenated hydrocarbon</td>
<td>5.4 ± 3.3</td>
<td>4.4 ± 2.3</td>
<td>6.2 ± 3.8</td>
<td>6.0 ± 1.9</td>
<td>10.7 ± 3.6</td>
<td>2.7 ± 1.4</td>
</tr>
<tr>
<td>OVOCs</td>
<td>4.6 ± 3.2</td>
<td>3.5 ± 2.7</td>
<td>5.1 ± 3.5</td>
<td>5.0 ± 2.4</td>
<td>9.7 ± 2.8</td>
<td>1.9 ± 1.1</td>
</tr>
</tbody>
</table>
3.2 Source appointment

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

Generally, T/B ≤ 2.2 indicates that VOCs are mainly influenced by transportation emissions (Wang et al., 2013; Yao et al., 2015), T/B > 8.8 indicates VOCs are mainly influenced by solvent use (Song et al., 2021), while other values indicates that VOCs are influenced by multiple emissions (Mo et al., 2015; Shi et al., 2015). The average T/B value was 1.0 ± 0.6 during the whole period, indicating the significant influence of transportation emissions in this study. In addition, isopentane/n-pentane concentration ratios of 0.6-0.8, 0.8-0.9, 2.2-3.8, and 1.8-4.6 for coal combustion, natural gas emissions, vehicle emissions, and fuel evaporation, respectively (Liu et al., 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, respectively (Russo et al., 2010; Zheng et al., 2018). The ratios of isopentane/n-pentane and isobutane/n-butane in this study were 1.33 and 0.50, respectively, suggesting that the concentration of VOCs were also influenced by fuel evaporation, 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.
Correlation analysis between specific VOC species

Figure 4 shows the chemical profiles of individual VOCs resolved by the PMF model during the entire observation period. After examining 3-6 factors, 20 base runs with 5 factors were eventually selected to represent the final result in four cases (Fig. S1). 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).

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). 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 a solvent usage source.

Factor 3 is characterized by relatively high levels of C2-C6 low-carbon alkanes (ethane, propane, isopentane, n-pentane, isobutane and n-butane), olefins (ethylene 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 components derived from vehicle-related activities. The contribution of methyl tert-butyl ether to this factor is also relatively high, and methyl tert-butyl ether is often 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 alkanes being on-road mobile sources (Bai et al., 2020). Therefore, factor 3 was 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

The results of source analysis of the whole stage, two pollution processes and 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 vehicular emission (24%) and combustion (23%). There were significant differences in the sources of VOCs for different pollution processes. The vehicular emission became the largest source during Case 1 (40%) and Case 3 (29%), consisting with large numbers of people going out after the blockade. Meanwhile, the contribution of 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 comparable value during all stages with a total value from 22% to 29%.
SOA has a significant impact on PM$_{2.5}$ pollution (Liu et al., 2021). The SOAFP 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 differences in concentrations. The top 10 VOCs contributed more than 95% to SOAFP generation, and the contribution of aromatic hydrocarbons was dominant with BTEX consistently occupying the top five positions and the largest contributor of toluene. The main sources of aromatic compounds are solvent use and industrial process emissions, similar to the result in other study (Wu et al., 2017). SOAFP values were 37 and 109 µg/m$^3$, respectively in Case 1 and Case 3. Among them, vehicular emission source had the highest SOAFP values (19 and 17 µg/m$^3$) and contributed 51% and 31%, in Case 1 and Case 3, respectively. Solvent usage source had the second highest SOAFP values (9 and 16 µg/m$^3$) with the contributions of 23% and 31%. Apart from that, combustion source in Case 3 (17 µg/m$^3$) was also abundant with a contribution of 31%. The contributions of industrial source (3.7 and 3.4 µg/m$^3$) and fuel evaporation (2.3 and 1.0 µg/m$^3$) were relatively low with values between 6-10% and 2-6% respectively. Therefore, the focus should be on the control of vehicular
emission, solvent usage as well as combustion for the control of PM$_{2.5}$ pollution in winter.

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

4. Conclusions

Continuous observation of VOCs during the infection of the Omicron epidemic 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 of PM$_{2.5}$ ranged from 54 to 239 µg/m$^3$ with an average value of $112 \pm 45$ µg/m$^3$ during the whole period. The daily average concentration of PM$_{2.5}$ during the sampling period is 0.7-3.2 times of the Grade II limit value in China, over 70% days exceeding 75 µg/m$^3$. The concentration of TVOCs ranged from 15.6 to 57.1 ppbv with an average of 36.1 ± 21.0 ppbv.

The values of PM$_{2.5}$ 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 staff” policy). The concentration of TVOCs in Case 1 and Case 3 were 48.4 ± 20.4 and 67.6 ± 19.6 ppbv, respectively, increased by 63% and 188% compared with values during clean days. The average concentrations of PM$_{2.5}$ and TVOCs during Case 3 were 1.3 and 1.8 times of the values in Case 1. The highest volume contributions of alkanes were found both in Case 1 (48%) and Case 3 (44%). Though the volume 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. Aromatics compounds are the main contributors to SOAFP, with BTEX being the main contributor during the entire period. SOAFP values reached 37 and 109 µg/m$^3$, respectively in Case 1 and Case 3.

Preliminary identification of local sources of contamination through T/B, 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 sources and urban area emissions. Five major pollution sources were obtained by the PMF receptor model, including industrial emissions (30%), vehicular emission (24%), combustion (23%), fuel evaporation (12%) and solvent use source (11%). There were 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 the contribution of industrial source decreased from 30% during the entire process to 23-25% during Case 1 and Case 3. Vehicular emission also had the highest SOAFP value (19 and 17 µg/m$^3$) followed by solvent usage (9 and 16 µg/m$^3$). Apart from that, combustion sources in Case 3 (17 µg/m$^3$) was also abundant with a contribution of 31%. The focus should be on the control of vehicular emission, solvent usage as well as combustion for the control of PM$_{2.5}$ pollution in winter.

Author contribution:

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Competing interests:

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

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