Measurement report: Intra-, inter-annual variability and source apportionment of VOCs during 2018-2020 in Zhengzhou, Central China

Shijie Yu [a,b], Shenbo Wang[b,c], Ruixin Xu [b,c], Dong Zhang [a,b], Meng Zhang [e], Fangcheng Su[b,c], Ruiqin Zhang [b,c]*, Lingling Wang [d]*

a. *College of Chemistry, Zhengzhou University, Zhengzhou 450001, China*

b. *Institute of Environmental Sciences, Zhengzhou University, Zhengzhou 450001, China*

c. *School of Ecology and Environment, Zhengzhou University, Zhengzhou   450001, China*

d. *Environmental Monitoring Center of Henan Province,Zhengzhou 450000*

e. *Pingdingshan Ecological Environment Monitoring Center of Henan Province, Pingdingshan 467000, China*

Correspondence to: Ruiqin Zhang (rqzhang@zzu.edu.cn) and Lingling Wang (Lindaw2007@126.com)

Abstract:

Ambient volatile organic compounds (VOCs) were measured continuously to investigate their characteristics, sources, atmospheric oxidation capacity (AOC) and chemical reactivity from January 2018 to December 2020 at an urban site in Zhengzhou, China. In this study, the total concentration of observed VOCs was 38.2±15.6 ppbv during the sampling period, with the characteristics that alkanes were the major VOC species, accounting for 60% of total VOCs. During the sampling period, the inter-annual variation of VOCs gradually reduced from 45.0±25.2 ppbv in 2018 to 36.7±22.0 ppbv in 2019, and to 30.5±15.4 ppbv in 2020. Ethane, ethene, and propane were the top three abundant species during the three-year observation period. The results showed that total AOC, dominated by OH radical reactions, was 7.4×10^7 molecules cm^{-3} s^{-1}. The total OH reactivity was 45.3 s^{-1}, and mainly contributed by NOx. The AOC and •OH reactivity exhibited well-defined seasonal and inter-annual patterns. Therefore, the control strategy should focus on key species among inter-annual and seasonal variations. Meanwhile, diagnostic ratios of VOC species indicated VOCs in Zhengzhou were greatly affected by vehicle emissions and liquefied petroleum gas/natural gas (LPG/NG). Positive matrix factorization analysis showed six sources were identified, consisting of industrial sources, solvent use, vehicle exhaust, LPG/NG, coal+biomass burning and biogenic sources. Vehicle emissions, solvent use and LPG/NG made the largest contributions to VOC emission in all three years. The proportion of the contribution of vehicle emissions and LPG/NG has increased with each passing year. However, the proportion of industrial and solvent sources presented a decreasing trend, which is speculated that the policy control effect is remarkable. The effect of VOCs on ozone formation suggests that vehicle emission and solvent utilization were still key sources. Therefore, it is necessary to formulate effective strategies for reducing ground-level O_3, and those sources mentioned above should be strictly controlled by the regulatory authorities.

1. Introduction

In recent years, regional atmospheric pollution has occurred frequently in the world. Many areas are suffering from severe haze episodes in autumn and winter, and O_3 pollution in summer (Li et al., 2019; Yan et al., 2018; Zhang et al., 2018). As volatile organic compounds (VOCs) are the important precursor of secondary pollutants such as ozone (O_3) and secondary organic aerosol (SOA), the study of VOCs is booming from the scientific community and governing bodies (Liu et al., 2019a; Song. et al., 2019c; Xu et al., 2017).

VOCs cover a large variety of species, and the chemical reactivity of each species varies greatly. Thus, VOC characteristics and active substance identification are a research priority. Alkanes were the dominant VOC species in many regions, while aromatics and alkenes were the largest contributors of ozone formation potential (OFP) (Li et al., 2019b; Yan et al., 2017). Yang et al. (2019) suggested that alkanes were the dominant group with 42% of the VOCs concentration, and C_2-C_3 hydrocarbons were the dominant substance in Wuhan. Huang and Hsieh (2019) studied the maximum incremental reactivity (MIR) and propylene-equivalent (PE) concentration, reporting toluene was the largest potential contributor to OFP, and industrial emissions contributed nearly 60% to OFP. Considering the complex composition of VOCs in the atmosphere, it is difficult to determine the sources of VOCs. Receptor models are widely used to apportion the source contributions of VOCs, including positive matrix factorization (PMF), chemical mass balance, and principal component analysis. In China, traffic emissions are often the main source of VOCs, particularly in major metropolitan areas (Li et al., 2019; Liu et al., 2019; Song, et al., 2019b). Moreover, industrial process and solvent utilization had remarkable influence on VOC emission (Hui et al., 2019; Mo et al., 2017). Biogenic sources also cannot be ignored due to the high reactivity, which contributed 5-20% of VOC emission (Wu et al., 2016). In addition to the study of VOCs characteristics and source apportionment, the analysis of atmospheric oxidation characteristics is a

73 current research hotspot. The variations in the AOC not only affect the O$_3$ level in

74 summer but also greatly impact the generation of secondary particles throughout the

75 entire year (Prinn, 2003). However, most of the related studies in China focused on

76 metropolitan areas, such as Beijing-Tianjin-Hebei (BTH) region (Gu et al., 2019b),

77 Pearl River Delta region (Zhang et al., 2015), and Yangtze River Delta region (Xu et

78 al., 2017; Zheng et al., 2020), but less research was carried on the heavily polluted

79 central plains. Meanwhile, previous studies are frequently used monitoring data in a

80 short time range, which can not reflect the comprehensive VOC pollution

81 characteristics in a region. Therefore, large-scale investigations should be

82 concentrated in central plains of China that has received limited attention in the past.

83  As the political and cultural center of Henan province, Zhengzhou has more than

84 10 million permanent residents and 4.0 million private vehicles in 2019 (Gu et al.,

85 2019a). This area is confronted with severe haze episodes and photochemical

86 pollution due to emit huge amounts of air pollutants (Li et al., 2020b). As a hot spot,

87 Zhengzhou has conducted a lot of research on air pollution, but many of those were

88 only focused on particulate matter (Jiang et al., 2018; Wang et al., 2019). There are

89 fewer studies on VOCs, especially the longer sampling time frames and seasonal

90 measurements in Zhengzhou. Through the adjustment of policies together with the

91 optimization of energy structure, the characteristics and sources of VOCs may be

92 significantly affected by a number of mitigation measures in recent years due to the

93 adjustment of policies and the optimization of energy structure. Therefore, it is

94 necessary to identify local VOC pollution characteristics based on a long time series

95 of monitoring data, which can provide a reference for the formulation of local air

96 pollution control measures.

97  To deepen the understanding of VOC pollution characteristics, chemical

98 reactivity and source contribution, three-year continuous VOCs data was measured

99 using online instruments in Zhengzhou from 2018 to 2020. The aims of this research

100 are: (1) analyze the variation characteristics of VOCs in Zhengzhou, including diurnal,

101 seasonal, and annual changes; (2) quantify the contribution of sources among intra-,

102 inter-annual variations and identify the locations of VOC sources; (3) parameterize

103 AOC and speciate OH reactivity; and (4) assess ozone formation by MIR and PE

104 analysis.

105

2. Methodology

2.1 Site and measurements

108   The observation period of this study is from January 2018 to December 2020.

109 VOC samples are collected at an urban site (34°45′N, 113°41′E) in the Department of

110 Environmental Protection of Henan Province. The surrounding environment was

111 mainly commercial and residential district, and there are traffic sources but no large

112 industrial source, which can represent a typical urban environment in Zhengzhou (Fig.

113 1).

114   The VOC species are continuously monitored by using an auto-GC system

115 (AMA Instruments GmbH, Germany). The specific information of this system was

116 described in Zou et al. (2015). The 57 VOC species (including 29 alkanes, 10 alkenes,

117 1 alkyne, and 17 aromatics) are calibrated by the VOC Standards of U.S. EPA PAMS

118 mixture (Spectra Gases, USA) before monitoring. During the observation period, zero

119 and span gas checks (PAMS calibration gases) were conducted monthly using the

120 5-point method, together with the adjustment of retention time. Data quality control of

121 this instrument is detailed in our previous study (Ren et al., 2020). The correlation

122 coefficient usually varied from 0.990 to 0.999, and the detection limits ranged from

123 0.02 to 0.12 ppbv, as shown in Table S1.

124   Meteorological data, such as atmospheric temperature (T), relative humidity

125 (RH), Ultra-Violet Ray (UV), precipitation (Pr), the planetary boundary layer height

126 (PBL), wind speed (WS) and direction (WD) were obtained from the surface

127 meteorological station of Henan monitoring center. Other trace gases datasets such as

128 the hourly NO, NO_2, CO, O_3, SO_2, and fine particles ($PM_{2.5}$) were obtained from the

129 ambient air quality observation station of Yanchang, which is about 2 km away from

130   the VOC monitoring station.

2.2 Positive Matrix Factorization model

132   In this paper, the model of U.S. EPA PMF 5.0 was used to identify the sources

133   and their contributions to VOCs (Gao et al., 2018; Norris et al., 2014; Song et al.,

134   2019a, 2019b; Yadav et al., 2019), and the details were showed in the supplement

135   (Text S1).

2.3 Relative reactivity of VOCs

137   To better understand the role of VOCs in the formation of troposphere O_3, OFP

138   and the PE concentration are investigated to analyze the chemical reactivity of VOC

139   species (Carter, 1994; Atkinson and Arey, 2003), and the detailed operation were

140   described in the supplementary materials (Text S2).

2.4 Atmospheric oxidation capacity and speciated oxidant reactivity

143   AOC is defined as the sum of the respective oxidation rates of primary pollutants

144   (e.g., CO, CH_4, and VOCs) by the oxidants (e.g., OH, NO_3 and O_3), and it can be

145   calculated by the Eq. (1) (Elshorbany et al., 2009; Xue et al., 2016).

$$AOC = \sum_i k_{Yi}[X][Y_i] \qquad (3)$$

147   Where $[X]$ and $[Y_i]$ are the number concentrations of molecule oxidant X and Y_i,

148   respectively; and k_{Yi} is the bi-molecular rate constant of molecule Y_i with oxidant X

149   (Zhu et al., 2020). In this paper, the reduced substances only included 57 PAMS

150   (provided by Spectra Gases Inc., USA) and CO. The oxidants only included •OH,

151   NO_3 and O_3 radicals. And the concentration OH and NO_3 radicals was estimated from

152   parameterization methods via Eq. (4) and Eq. (5) (Carter, 1994; Warneke, 2004).

$$[OH] = a \times (J_{O^1D})^{\alpha} \times (J_{NO_2})^{\beta} \times \frac{b \times [NO_2] + 1}{c \times [NO_2]^2 + d \times [NO_2] + 1} \qquad (4)$$

154 Where J_{O1D} and J_{NO2} are measured photolysis frequency (s^{-1}) of ozone and NO$_2$,

155 respectively. The value of a, b, c, α, β is 4.1×10^9, 140, 0.41, 1.7, 0.83 and 0.19,

156 respectively (Yang et al., 2019).

157 NO$_3$ concentration in the atmosphere is based on the steady-state assumption

158 (Liebmann et al., 2018).

159 $$[NO_3] = \frac{k_{NO_2} \times [NO_2] \times [O_3]}{J_{NO_3} + J_{NO+NO_3} \times [NO] + \sum_i k_{NO_3+VOC_i} \times [VOC]_i} \qquad (5)$$

160 Where J_{NO3} is the measured photolysis frequency (s^{-1}) of NO$_3$. The rate

161 coefficients for NO$_2$ -O$_3$ (k_{NO2+O3}) and NO-NO$_3$ (k_{NO+NO3}) were obtained by Atkinson

162 et al. (2004). A detailed description of the calculation processes of OH and NO$_3$ have

163 been provided in previous study (Yang et al., 2021).

164 Additionally, OH reactivity is another indicator of atmospheric oxidation. It is

165 the inverse of the OH lifetime and defined as the product of the rate coefficients and

166 the concentrations of the reactants with OH. OH reactivity is calculated by Eq. (6)

167 (Mao et al., 2010):

168 $$OH\ reactivity = \sum k_{OH+VOC_i} \times [VOC_i] + k_{OH+CO} \times [CO] + k_{OH+NO} \times [NO] + k_{OH+NO_2} \times [NO_2]$$

169 $$+ k_{OH+SO_2} \times [SO_2] + k_{OH+O_3} \times [O_3] + k_{OH+other} \times [other] \qquad (6)$$

170 Where *[Xi]* is the concentration of species (e.g., CO, NOx, SO$_2$ and VOCs), and

171 the rate coefficients k_{OH} (in cm^3 molecule1 s^{-1}) represents the corresponding reaction

172 rate coefficients.

2.5 CPF analysis

174 The CPF was developed to identify potential source contributions by using the

175 PMF source contribution solution, coupled with the account of wind direction (Guo et

176 al., 2011; Hsu et al., 2018; Wu et al., 2016). The CPF is defined as:

$$CPF = \frac{m_{\triangle\theta}}{n_{\triangle\theta}}$$

177 Where $m_{\triangle\theta}$ is the number of appearances from wind sector $\triangle\theta$ (each is 22.5°)

178 that exceeds the concentration threshold (75th percentile of each source contribution)

179 and $n_{\triangle\theta}$ is the total number of occurrence in the same wind sector. Weak winds (< 1.5

180 m s^{-1}) were excluded from the calculation because of their difficulty in defining the

181 wind direction (Zheng et al., 2018).

3. Results and discussion

3.1 Characteristics of VOCs in Zhengzhou

3.1.1 concentrations and compositions of VOCs

185 Average ambient VOC concentrations and chemical species measured in

186 Zhengzhou are shown in Table S2. The annual average concentration of VOCs was

187 38.2±15.6 ppbv, close to the concentrations in Langfang (33.4 ppbv) (Song et al.,

188 2019a) and Wuhan (32.6 ppbv) (Yang et al., 2019), lower than that in Nanjing (43.5

189 ppbv) (An et al., 2014), Guangzhou (42.7 ppbv) (Zou et al., 2015), Mexico (84.0 ppbv)

190 (Garzn et al., 2015), and higher than that in Guilin (23.7 ppbv) (Zhang et al., 2019),

191 London UK (22.2 ppbv) (Schneidemesser et al., 2010) and Metropolitan Vancouver

192 (19.2 ppbv) (Xiong et al., 2020). Alkanes were the major components of VOCs with a

193 mean concentration of 23.0±19.5 ppbv, accounting for 60% of total VOC

194 concentration, followed by alkenes (19%), aromatics (14%), and alkynes (7%). Many

195 previous studies have found that alkanes were the dominant group (Fu et al., 2020; Gu

196 et al., 2020), similar to that in Zhengzhou.

197 To clarify the characteristics of VOC emission sources, Table 1 lists the

198 concentrations of the 20 most abundant species, accounting for 90% of the VOCs.

199 During the sampling period (2018-2020), the most important VOC species in

200 Zhengzhou were ethane (8.8±5.0 ppbv), ethylene (4.7±4.0 ppbv), propane (4.2±2.5

201 ppbv), acetylene (2.6±3.3 ppbv), and n-butane (2.3±1.7 ppbv). In general, C$_2$-C$_4$

202 species are closely related to vehicular exhausts, coal burning, and LPG (Hui et al.,

203 2021; Zhang, et al. 2020). Among the most abundant 20 VOC species , half of them

204 were alkanes, occupying 91% of the total alkanes measured. The C$_2$-C$_3$ alkanes are

205 mainly originated from LPG, while C$_4$-C$_5$ alkanes are considered as the tracer for

206   vehicle emissions (Fan et al., 2021). The most abundant alkene species were ethylene,

207   propene, isoprene, and 1-butene, representing 93% of the total alkanes. C_2-C_4 alkenes

208   mainly come from vehicle exhausts and LPG (Zhang et al., 2015), whereas isoprene is

209   a typical biogenic tracer (Maji et al., 2020). There are five aromatics in the 20 most

210   abundant species, including BTEX (benzene, toluene, ethyl-benzene, and xylenes)

211   and styrene. Those aromatics are the most frequently observed aromatic compounds

212   in urban areas, which are originated from vehicle exhausts, industrial processes,

213   solvent usage, and combustion sources (Hui et al., 2019).

3.1.2 Inter-annual variation of VOCs

215   The inter-annual average concentrations and contributions of VOCs during 2018

216   to 2020 are shown in Table S2. The inter-annual variation of VOCs gradually reduced

217   as follows: 45.0±25.2 ppbv (in 2018), 36.7±22.0 ppbv (in 2019), and 30.5±15.4 ppbv

218   (in 2020). The decrease trend of VOCs could be attributed to the increasingly

219   stringent policies for emission reduction and the influence of COVID-19 lockdown on

220   air quality in 2020 (Wang et al., 2021a).

221   The concentrations of the 20 most abundant species are listed in Table 1. Ethane,

222   ethene, and propane were the top three abundant species during all three years, which

223   is speculated that LPG and vehicular exhausts had a significant impact on the

224   surrounding area of the sampling site (Yadav, et al. 2019). C_4-C_5 alkanes and some

225   aromatics were the main tracers of motor vehicle exhaust, (Fan et al., 2021). However,

226   those species were cut down in 2020, which might be affected by the epidemic. As a

227   tracer of coal burning, acetylene was gradually decreased from 4.3±4.3 ppbv in 2018

228   to 0.7±0.8 ppbv in 2020.

3.1.3 Seasonal variations

230   As plotted in Fig. S2 and Table S3, the monthly mean mixing ratios of VOCs

231   and its compounds were investigated. VOCs showed a clear seasonal dependence with

232   a highest concentration in winter (50.0 ppbv) followed by spring (38.4 ppbv), autumn

233 (32.5 ppbv) and summer (26.1 ppbv). Meanwhile, the seasonal variations in the group

234 of alkanes, alkenes, alkynes, and aromatics were similar to VOCs. In addition, the

235 monthly mean mixing ratios of dominant and tracer species were plotted in Fig. 2.

236 The results showed that almost all VOCs had a clear seasonal dependence, which

237 were shown as highest concentration in winter while lowest concentration in summer.

238 However, the mixing ratios of isoprene were highest (0.82 ppbv) in July and lowest

239 (0.11 ppbv) in December. As the tracer of biogenic source, isoprene showed a positive

240 correlation with temperature (R^2=0.61, p<0.01). Besides biogenic emission, the

241 seasonal VOC variation was mainly influenced by the changes of anthropogenic

242 sources. As a northern city of China, Zhengzhou emits a lot of pollutants during the

243 heating season in winter (Wang et al., 2019). The higher concentration of VOC and

244 tracers (such as acetylene and aromatics) in winter may be derived from coal

245 combustion (Zhang et al., 2020).

246   Seasonal variations in VOCs concentrations were associated with several factors,

247 such as photochemical activities and meteorological conditions. In summer, VOC is

248 consumed under the condition of high temperature, strong light radiation, and high

249 concentration of OH radicals (Huang et al., 2019). In winter, the high level of VOCs

250 can be attributed to lower boundary layer and calm weather conditions (Hui et al.,

251 2019). In addition, the pollution transmission from BTH region cannot be ignored

252 because that the north wind prevails in Zhengzhou in winter. The seasonal variation of

253 VOCs in several cities was investigated and the variation trend of VOC

254 concentrations in most studies were similar to that in Zhengzhou (Liu, et al., 2019;

255 Yadav et al., 2019).

3.1.4 Diurnal variations

257   The diurnal variations in VOCs, trace gases (NO$_2$ and O$_3$), and meteorological

258 parameters (T, RH, WS, and UV) are shown in Fig.S3. The VOCs presented a reverse

259 trend with O$_3$ (R^2=−0.82, p < 0.01), whereas the diurnal variation in VOCs showed

260 moderate consistency with the variations of NO$_2$ (R^2= 0.62, p < 0.01). The high values

261   of VOCs generally appeared in the morning with low O_3 concentrations. The peak in

262   the morning was attributed to vehicle emission (Li et al., 2019b). In addition, local

263   meteorology and atmospheric processes also played important roles in the diurnal

264   variations of VOCs in ambient air. In the early morning, VOC remained at a high

265   concentration due to the stable atmospheric condition and shallow boundary layer

266   height (Hui et al., 2020). The value of VOCs declined to the lowest value (26.7 ppbv)

267   at 15:00 China standard time (CST), in which O_3 reached a maximum level as the

268   production rate of O_3 and the consumption rate of O_3 reached equilibrium. In the

269   afternoon, high temperature and light radiation intensity led to the consumption of

270   VOCs. Meanwhile, higher wind speed also accelerated the diffusion of VOCs.

271   Afterward, VOC concentration gradually accumulated with the arrival of the late

272   traffic peak, and keep a high level throughout the night. It should be noted that VOC

273   concentrations at night were generally higher than those during the day. Previous

274   studies have suggested that VOC can be oxidized by O_3,OH radicals and NO_3

275   radicals (Atkinson and Arey, 2003). During the daytime, the reactions with OH

276   radicals and O_3 are the most important chemical reactions for VOCs, while the

277   reactions with NO_3 radicals and O_3 are the main sedimentation reactions occurring at

278   night. VOCs concentrations were generally higher at night because the chemical

279   activity of OH radicals is much higher than that of NO_3 radicals (Carter, 2010).

280   The mean diurnal variations of high concentration and tracer VOCs were

281   investigated, as shown in Fig. 3. As tracers of motor vehicle exhaust (Zheng, et al.

282   2018), Iso/n-pentane had a remarkable peak at 8:00 CST, which is suggested to be

283   vehicle emissions. Meanwhile, BTX and C_2-C_4 alkanes also represented similar

284   diurnal variation characteristics, which was speculated to be greatly affected by motor

285   vehicles. However, the mixing ratio of isoprene showed higher values in the afternoon

286   and had a similar trend with temperature. The elevated values of isoprene in the

287   afternoon indicated significant emissions from biogenic sources.

3.2 Diagnostic ratios

Some of the VOC species are commonly used as indicators for emission sources. To characterize the differences in the contribution of various sources in four seasons, the ratio of B/T (benzene/toluene) and *i*-pentane / *n*-pentane have been used as the preferred metric in this study.

The ratio of B/T can be used to distinguish potential sources such as traffic emission, coal+biomass combustion and solvent usage. Diagnostic ratios varied according to the emission sources (i.e., below 0.20 for solvent usage, 0.5 for traffic source, 1.5-2.2 for coal combustion, and 2.5 for biomass burning). (Huang et al., 2019; Li et al., 2019a). As shown in Fig. S4, the highest value of the B/T ratio was 0.55 in winter, suggesting traffic emissions had affected the atmosphere. Meanwhile, the ratios are 0.31, 0.27, and 0.31 in spring, summer, and autumn, respectively, indicating it is more likely the aromatic derived from the mixed sources of solvent usage and vehicle source during these seasons. As a transportation hub, Zhengzhou has a large number of motor vehicles (Gu et al., 2019a). Therefore, the region needs to strengthen the control of motor vehicle.

The ratio of i-pentane to n-pentane was also investigated. i-Pentane and n-pentane have similar reaction rates with the OH radicals and the ratios of these pair species indicated different sources. Pentanes always originated from the consumption of coal combustion, vehicle emissions, and fuel evaporations with the ratio range of 0.56–0.80, ~ 2.2, and 3.8, respectively (Huang et al., 2019; Li et al., 2019a). The highest ratio of *i*-pentane / *n*-pentane was found in summer (2.79), indicating strong impacts of traffic sources. The ratio was 1.88 in spring and 1.96 in autumn, which suggested that most of VOCs originated from the mixed sources of vehicle emissions and coal combustion. In addition, the average ratios in winter (1.55) was lower than the other three seasons, indicating the comparatively stronger contribution from coal burning in the heating season.

3.3 Source apportionment by PMF model

3.3.1 Source identification

Six sources, namely industrial sources, solvent use, vehicle exhaust, LPG/NG, coal+biomass burning and biogenic sources were identified by the PMF model. The source profiles of VOCs during the sampling period are presented in Fig.4.

Both sources 1 and 2 were characterized by a high percentage of C_6-C_8 alkanes and aromatics, which were major components emitted from various solvents or industrial processes (Zhou et al. 2019, Wang et al. 2021). However, source 1 was also rich in ethylene and propylene, which indicated the raw materials or products of chemical manufacturing processes (Fan et al. 2021, Hui et al. 2021). In addition, this source had correlations with gas tracers of NO_2, SO_2, and CO (R^2=0.42, 0.37, and 0.44, respectively). Meanwhile, source 2 appeared to exhibit poor correlations with gas tracers (R^2<0.10). Therefore, source 1 was assigned to industrial sources, while source 2 was identified as solvent use.

Source 3 contained higher levels of C_4-C_6 alkanes and aromatic. It is reported that i-pentane were usually originated from gasoline evaporation (Mo et al. 2017), and the other species are all associated with vehicle exhausts (Zheng et al. 2021). A ratio of T/B was 2.0 in this profile, which further confirmed the effect of vehicular emissions (Yao et al. 2021). In addition, the source correlated significantly with CO and NO_2 (p<0.01), but not with SO_2 (p>0.05). Therefore, source 3 was identified as vehicle exhaust.

Source 4 was dominated by a strong presence of ethane, propane, propylene, and i/n-butane, which can also release from fuel evaporation (gasoline and LPG/NG) (Zhang et al. 2019). In particular, the aromatics of this source were very low. Similar to factor 3, the source did not correlate with SO_2 (p>0.05), but had a positive correlation with CO and NO_2 (p<0.01). Therefore, this source was considered as LPG/NG.

The fifth source was distinguished by significant amounts of acetylene (72%),

343   which is a marker of combustion sources (Hui et al. 2021). In addition, the source was

344   also characterized by a significant amount of benzene and C_2-C_3 hydrocarbons, which

345   are representative species of coal and biomass burning (Zheng et al. 2021).

346   Meanwhile, the independent traces (i.e., NO_2, SO_2, and CO) exhibited correlations

347   with this factor ($p<0.01$, $R^2 >0.3$). Therefore, source 5 was considered to be

348   coal+biomass burning.

349   Source 6 exhibited a significantly high composition of isoprene, which mainly

350   produced by vegetation through photosynthesis (Song et al. 2019a). Accordingly,

351   source 6 was labeled as biogenic source.

3.3.2 Inter-annual variation

353   The concentration contributions of each VOC source during 2018-2020 are

354   shown in Fig.5. In 2018, vehicular exhaust was the largest contributor to VOC mixing

355   ratios (28%), followed by solvent utilization (27%), LPG/NG (17%) and industrial

356   sources (15%). The contribution of coal+biomass burning and biogenic source

357   accounted for 8% and 5% of the total VOC concentration, respectively. As for 2019,

358   vehicle emissions made the largest contribution (33%) to atmospheric VOCs. The

359   second most significant source was solvent utilization, accounting for 24% of the total.

360   The contribution of LPG/NG, industrial sources, coal+biomass burning, and biogenic

361   source to atmospheric VOCs were 16%, 14%, 10% and 3% in 2019. While vehicular

362   exhaust, solvent use, LPG/NG, industrial sources, coal+biomass burning and biogenic

363   source occupied 33%, 21%, 20%, 13%, 9% and 4% in 2020, respectively.

364   In summary, vehicle emissions, solvent use and LPG/NG made the largest

365   contributions in all three years. Meanwhile the proportion of vehicle emissions and

366   LPG/NG has increased with each passing year. As a famous transportation hub city,

367   the number of motor vehicles in Zhengzhou maintain the annual growth of 0.4 million

368   during the past five years, and has exceeded 4.5 million in 2020 (Gu et al., 2019a).

369   Thus, vehicle exhaust was an important source of ambient VOCs at Zhengzhou.

370   LPG/NG are widely used in residential life, industrial production, and motor vehicle.

371 Combined with the actual situation of the site, residential emissions may be the main

372 source of LPG/NG. With the adjustment of energy structure, most industrial

373 enterprises and taxis in Zhengzhou have used NG as energy or fuel. It should be

374 pointed out that the proportion of industrial and solvent sources presented an annual

375 down trend. In recent years, Zhengzhou City has carried out special actions for VOC

376 emission reduction, focusing on the control of industrial and small scattered pollution

377 enterprises. According to the results of the PMF model, it is speculated that the effect

378 of policy control is remarkable.

379 The source contributions determined in this study were also compared with other

380 researches. Table 2 shows the source apportionment of VOCs was basically within the

381 values reported for other Chinese cities (Huang et al., 2019; Hui et al., 2018; Li et al.,

382 2020c; Mo et al., 2017; Yan et al., 2017). It was found that traffic emission is the

383 main source of VOCs in Zhengzhou and other seven cities, which indicated that

384 vehicle emission has a great impact on the concentration of VOCs in urban

385 atmosphere. It should be noted that the contributions of each source in this study were

386 very similar to those of Wuhan (Hui et al., 2018). Considering that Zhengzhou and

387 Wuhan are both important transport hub cities in Central China, the result is in line

388 with expectations.

389 3.3.3 Seasonal variation

390 Due to the different meteorological conditions and emission strengths, source

391 contributions were variable in different seasons. As shown in Fig.6, the seasonal

392 variations of biogenic emissions were significant, with the high contribution in

393 summer (8%) and the lowest value in winter (<1%). This might be affected by both

394 temperature and light intensity. Contrarily, the contributions from coal+biomass

395 burning and LPG/NG were larger in winter and lower in summer. Combustion

396 sources accounted for a larger proportion of emissions in winter (14%), while only

397 4% in summer. It should be pointed out that LPG accounted for a relatively high

398 concentration in winter along with the continuous promotion of coal to gas conversion.

399   Meanwhile, industrial emissions contributed to a high percentage of the VOCs in

400   spring (21%) but exhibited a low value in autumn (12%). In addition, motor vehicle

401   emissions have no obvious seasonal characteristics, and the contribution rate to the

402   atmosphere in four seasons exceeded 20% of the VOCs, indicating that motor

403   vehicles had a great impact on the air quality of Zhengzhou.

404 3.3.4 CPF and daily variation of each source

405   To examine the source orientation and time series of each source, CPFs and

406   diurnal variation are provided in Fig. 7.

407   CPF plots indicated the biogenic sources mainly originated from the north

408   direction with conditional probability (CP) values of approximately 0.37. It is mainly

409   affected by the plant emission in the northern suburbs and the urban greening in the

410   sampling area. In addition, the diurnal patterns of biogenic source showed an obvious

411   T dependence, with the highest concentration at midday, might due to photosynthesis

412   activity. The CPF plots also showed coal+biomass burning and industrial source

413   originated from the northeast and south direction. The diurnal variation in combustion

414   source was characterized by an apparent increase at night, which is related to the

415   accumulation of pollutants during night heating. Moreover, the highest VOC

416   concentration from the industrial source was observed at 10:00 CST, probably due to

417   the industrial activities during the daytime. CPF plots for solvent use indicated these

418   sources were located at the southeast of the monitoring station. Meanwhile, the

419   LPG/NG source displayed higher contributions from the north and east direction,

420   associated with resident activities around the sampling site. The vehicle emissions

421   were related to all directions, which might come from the emission of dense road

422   network around the station. The diurnal pattern of traffic source was characterized by

423   two peaks in the morning and evening derived from traffic rush hours.

424 3.4 AOC

425   During the sampling periods, AOC was quantified and shown in Fig.8. The

426   calculated averaged value of total AOC was 7.4×10^7 molecules cm^{-3} s^{-1}, which was

427   comparable to those reported in a suburban site between Beijing and Tianjin (Yang et

428   al., 2020b), but significantly higher than those observed in Shanghai (Zhu, et al. 2020),

429   Hong Kong (Xue et al., 2016), Chile (Elshorbany et al., 2009) and Berlin (Geyer et al.,

430   2001). Among AOC categories, OH exhibited the highest average concentration (7.0

431    $\times 10^7$ molecules cm^{-3} s^{-1}), accounting for 95% of the total AOC, followed by O_3 (3.4

432    $\times 10^6$ molecules cm^{-3} s^{-1}) and NO_3 (1.1×10^5 molecules cm^{-3} s^{-1}, which contributed

433   to 4% of the total AOC. Thus, OH is the main contributor of the atmospheric

434   oxidation in Zhengzhou, and similar results have been reported by other studies (Yang

435   et al., 2021; Zhu et al., 2020).

436   During 2018-2020, the total AOC presented decreasing trend annually (as shown

437   in Fig.8), with the mean values of 8.0, 6.4 and 6.2×10^7 molecules cm^{-3} s^{-1},

438   respectively. As expected, OH was the predominant oxidant in all three years, with

439   95%, 95% and 97% of the total AOC, respectively. The primary pollutants (eg., CO,

440   CH_4, and VOCs) decreased significantly in 2020 due to large reductions in economic

441   activities and associated emissions in COVID-19 lockdown. However, the average

442   concentration of OH was highest in 2020 (4.8×10^7 molecules cm^{-3}), which is far

443   higher than that of the previous two years. Thus, the level of atmospheric oxidation

444   needed additional attention. It should be noted the oxidation of the atmosphere has not

445   decreased or even increased significantly during the epidemic, which has been

446   reported by many researches (Wang et al., 2021b).

447   As shown in Fig. S5, the mean AOC values showed pronounced seasonal

448   variations. The highest total AOC value was detected in summer (7.5×10^7 molecules

449   cm^{-3} s^{-1}), followed by winter (6.4×10^7 molecules cm^{-3} s^{-1}), spring (5.8×10^7

450   molecules cm^{-3} s^{-1}) and autumn (5.7×10^7 molecules cm^{-3} s^{-1}). The concentration of

451   OH in summer was significantly higher than that in other seasons, which can be

452   ascribed to relatively favorable meteorological conditions. Meanwhile, the high

453   isoprene concentrations were observed in summer, and its high reaction rate

454   coefficients with the oxidants (eg., OH, NO_3 and O_3) revealed a highly oxidative

455   environment during the summer campaign in Zhengzhou. This seasonal pattern of the

456   AOC were similar with those of other studies conducted at the national level, urban

457   and suburban environments (Yang et al., 2021; Li et al., 2020a).

3.5 Atmospheric environmental implications

458

3.5.1 OH reactivity of measured species

459

460   The calculated OH reactivity was categorized into SO_2, NO_2, NO, O_3, CO and

461   VOCs and shown in Fig.9. During the sampling period, the average values of the total

462   OH reactivity was 45.3 s^{-1}. In general, the OH reactivity assessed in this paper was

463   much higher than those determined in Shanghai (Tan et al., 2019), Chongqing (Tan et

464   al., 2019), Shanghai (Zhu et al., 2020) and New York (Ren et al., 2006), but was

465   comparable or lower than those in Xianghe (Yang et al.,2020a) and Backgarden (Lou

466   et al., 2010). In Zhengzhou, NO_2 made the largest contribution to the total OH

467   reactivity (54%), followed by VOCs (17%), NO (16%), CO (11%), SO_2 (3%) and O_3

468   (1%). Similar results have also been reported in previous studies conducted in other

469   regions (Yang et al.,2021). It should be pointed out that this paper only calculated the

470   OH reactivity of measured species, but did not involve unmeasured species, such as

471   secondary products (OVOCs and nitrates produced by photochemical reactions) and

472   monoterpenes. Therefore, the value of OH reactivity in this study was underestimated

473   to a certain extent.

474   The detailed contribution of each VOC group to the total OH reactivity were

475   presented in Table S4 and Table S5. The OH reactivity of total VOCs was 8.1 s^{-1},

476   which was much lower than those in Beijing (11.2 s^{-1}) and Heshan (18.3 s^{-1}) (Yang et

477   al., 2017), but close to that t in Xianghe (7.9 s^{-1}) (Yang et al., 2020). The contribution

478   of alkenes to OH reactivity was predominant, accounting for 5.2 s^{-1} of the total OH

479   reactivity of VOCs. During the sampling period, isoprene attained the largest

480   contribution to the OH reactivity of the total VOCs, followed by ethene, m/p-xylene,

481   propene, styrene, cis-2-butene, trans-2-butene, toluene, i-pentane and trans-2-pentene,

482   collectively accounting for 70% of the OH reactivity towards the total VOCs.

483   As shown in Fig.9, the OH reactivity showed significant inter-annual and
484   seasonal variations. The statistical results exhibit decreasing trend of OH reactivity
485   during 2018-2020 in Zhengzhou, with the mean values of 51.1, 46.9, and 36.9 ppbv,
486   respectively. The trend might due to emission reduction measures, such as
487   traffic-related emissions and the "Coal to Gas" project. The OH reactivity value in
488   2020 was 21% lower than that in the previous year, which is closely related to the
489   emission reduction as a result of COVID-19. As for seasonal variations, the mean
490   values were in the order of winter ($74.5 \ s^{-1}$) > autumn ($48.6 \ s^{-1}$) > spring ($43.1 \ s^{-1}$) >
491   summer ($29.0 \ s^{-1}$). The notably difference might be attributed to the higher reactive
492   trace gas loadings, especially in NOx and CO. As a northern city, coal combustion in
493   heating season in Zhengzhou produces higher concentrations of NOx and CO, leading
494   to higher OH reactivity. Therefore, we should continually strengthen the control of
495   trace gases, especially in autumn and winter. The OH reactivity of total VOCs was
496   close, with higher value in winter ($7.3 \ s^{-1}$) and lower in autumn ($5.3 \ s^{-1}$). However,
497   the concentrations of key species were significantly different among the four seasons.
498   Ethylene and propylene had highest OH reactivity in winter, which is speculated to
499   the emission of combustion sources. In addition, Isoprene made the largest
500   contribution to the total OH reactivity in summer and spring, proving significantly
501   affected by biogenic source. Overall, the research on specific OH reactivity clearly
502   elucidated the seasonal and annual variations of major reactants. Therefore, the
503   control strategy based on OH reactivity should focus on key species.

3.5.2 The effect of VOCs on ozone formation

505   Since VOCs are important precursors of O_3 formation in the ground-level
506   atmosphere, it is necessary to adequately estimate the contribution of each VOC
507   species to ozone formation. Fig. S6 shows the concentration contributions of the four
508   VOCs categories expressed on different scales from 2018 to 2020. The result
509   suggested aromatics made the largest contribution of the MIR concentration,
510   accounting for the combined ratios of 81%. Meanwhile, alkenes were the largest

511   contributors to PE concentration (87%). Although the concentrations of aromatics and

512   alkenes were relatively low, these two VOC groups played an important role in ozone

513   formation. This result is supported by many previous studies (Hui et al.,2021; Li et al.,

514   2020b).

515   Among the top 10 reactive species contributed to Propy-Equiv and MIR

516   weighted concentrations (as shown in Fig.10), eight compounds were the same,

517   differing only in their rank order. The top 10 VOCs obtained from the two methods

518   represented 67% and 74% of VOCs respectively. Considering the kinetic activity,

519   isoprene ranked first with the PE method of 8.8 ppbC, accounting for approximately

520   20% of the total PE concentration. m,p-Xylene, styrene, ethene, and toluene ranked

521   the second to fifth based on the PE method, explaining 16%, 10%, 7%, and 5% of the

522   total OFP, respectively. In comparison, ethene, m,p-xylene, toluene, propane, and

523   isoprene had highest MIR concentrations, which accounted for about 23%, 21%, 12%,

524   7%, and 7%, respectively. The results in this study highlighted the contributions of

525   isoprene ethene, m, p-xylene, and toluene to the ozone formation, and these three

526   species are mainly emitted from vehicle exhaust and industrial coatings (Xiong and

527   Du, 2020).

528   Based on the results of source apportionment, the source contributions to OFP

529   and PE were calculated (shown in Fig. S7). Vehicle emission made the greatest

530   contribution to ozone formation, followed by solvent utilization (PE:25%; OFP:29%).

531   Besides, the contribution of biogenic emissions cannot be ignored, occupying 23% of

532   total PE. As the result of the discrepancy between the MIR weighted and PE weighted

533   concentrations, the contribution of this source to OFP was relatively low, only

534   accounting for 7%. The PE concentration method only considers the kinetic reactivity

535   of VOC species but ignores the mechanism reactivity, while the MIR method takes

536   the ratio of VOC/NOx on the ozone formation into consideration.

4. Conclusions

537

538   In this study, the hourly data of 57 VOC species were collected during 2018 to

539   2020 at an urban site in Zhengzhou, China. The results showed that the average total

540   VOC mixing ratios were 38.2±15.6 ppbv, and the VOC concentrations were

541   dominated by alkanes (60.2%) among the three years. During the sampling period, the

542   inter-annual variation of VOCs gradually reduced as follows: 45.0±25.2 ppbv (in

543   2018), 36.7±22.0 ppbv (in 2019), and 30.5±15.4 ppbv (in 2020). VOCs showed a

544   clear seasonal dependence with the highest in winter (50.0 ppbv) and lowest in

545   summer (26.1 ppbv). Based on PMF method, 6 sources were identified as vehicle

546   exhaust (31%), solvent use (24%), LPG/NG (18%), industrial sources (14%),

547   coal+biomass burning (9%) and biogenic source (4%). The proportion of vehicle

548   emissions and LPG/NG has increased with each passing year. However, the

549   proportion of industrial and solvent sources presented a decreasing trend. In addition

550   to significant inter-annual variation, the sources of VOCs also showed seasonal

551   differences. As for vehicle emissions, the contribution to the atmosphere in four

552   seasons was more than 20%. VOCs are significantly affected by combustion sources

553   (14%) in winter, while the influence of plant sources cannot be ignored (8%) in

554   summer.

555   Meanwhile, this paper focuses on the atmospheric environmental implications of

556   VOCs, including AOC, the OH reactivity and OFP. During sampling periods, the

557   campaign-averaged value of the total AOC was 7.4×10^7 molecules cm^{-3} s^{-1}, and OH

558   exhibited the highest average concentration, accounting for 95% of the total AOC.

559   The average value of the total OH reactivity was 45.3 s^{-1}, and NO$_2$ made the largest

560   contribution to the total OH reactivity (54%), followed by VOCs (17%), NO (16%),

561   CO (11%), SO$_2$ (3%) and O$_3$ (1%). The effect of VOCs on ozone formation were

562   investigated. Although the concentration of aromatics and alkenes were relatively low,

563   they played an important role in ozone formation. Ethene, m, p-xylene, and toluene

564   contributed significantly to the ozone formation in Zhengzhou. Based on the results of

565   source apportionment, vehicle emission and solvent utilization were still key sources

566   of VOCs that contribute to ozone formation.

567   Overall, the research of concentrations, source apportionment and atmospheric

568   environmental implications clearly elucidated the differences in major reactants

569   observed in different seasons and years. Therefore, the control strategy should focus

570   on key species and source among inter-annual and seasonal variations. The results can

571   provide references for local governments to develope control strategies of VOCs

572   during O$_3$ pollution events.

573

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574

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Figure list

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Fig. 1 Locations of the sampling stations, and Fig. a-c represents China, Henan and Zhengzhou respectively.

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873 **Fig. 2** Monthly changes in the concentrations of the typical VOCs species in

874 Zhengzhou. The upper and lower boundaries of the boxes indicate the 75th and 25th

875 percentiles, respectively; the lines within the boxes mark the median; the whiskers

876 above and below the boxes indicate the 90th and 10th percentiles, respectively.

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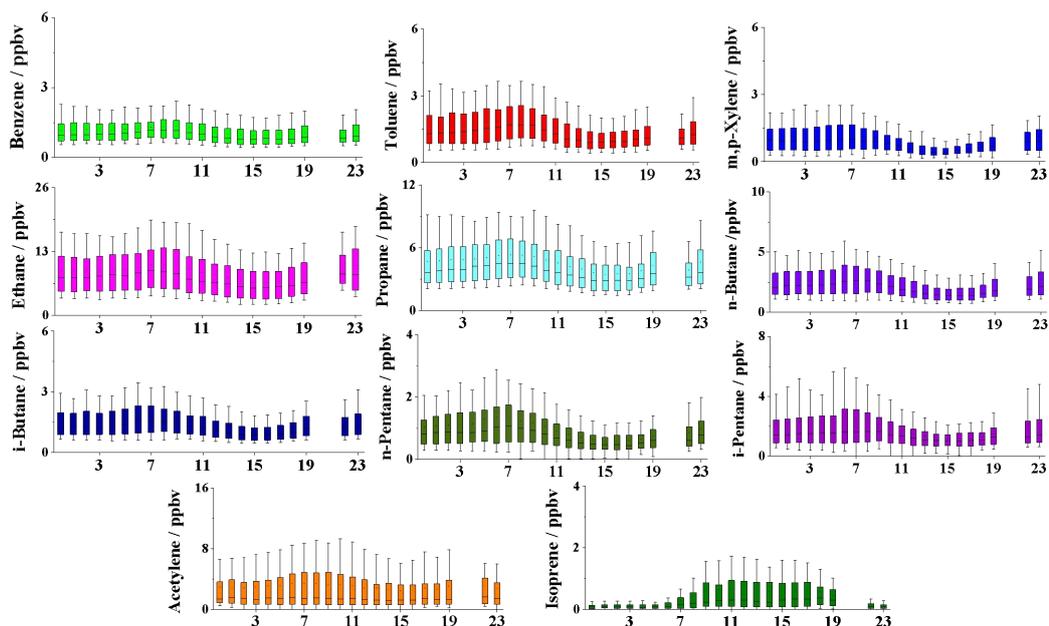
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880 **Fig. 3** Diurnal variations in VOCs compounds measured at Zhengzhou. The upper and

881 lower boundaries of the boxes indicate the 75th and 25th percentiles, respectively; the

882 lines within the boxes mark the median; the whiskers above and below the boxes

883 indicate the 90th and 10th percentiles, respectively.

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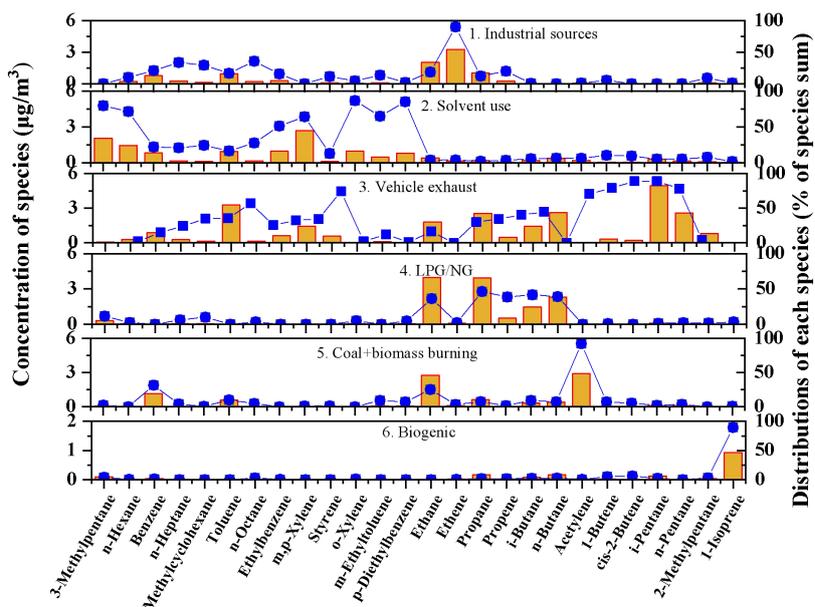
Fig.4 Source profiles and contribution percentages during the observation period by
PMF model (bar is a mixing ratio and dot is a percentage).

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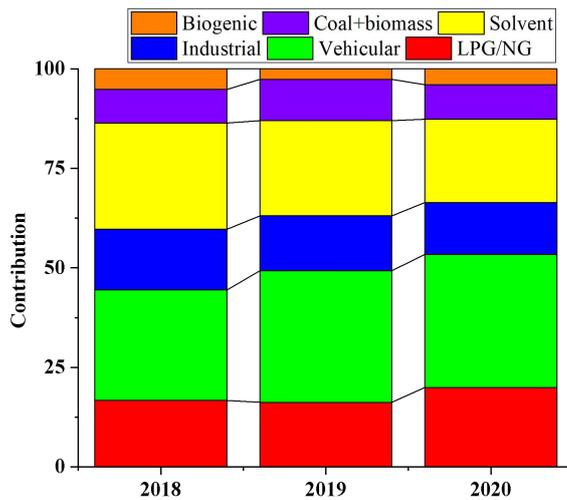
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890   **Fig. 5** The contributions of each VOC source during 2018-2020.
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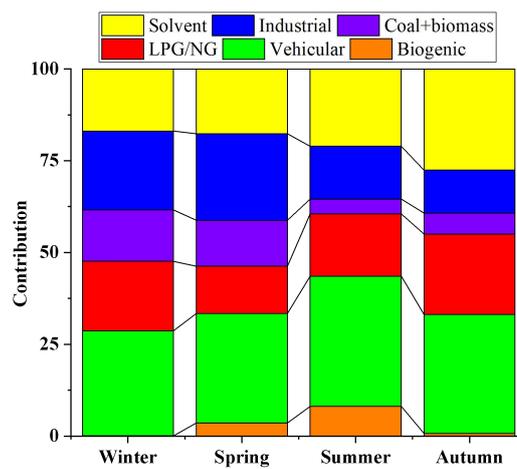
895 **Fig. 6** Seasonal variation of source contributions to VOCs concentration.

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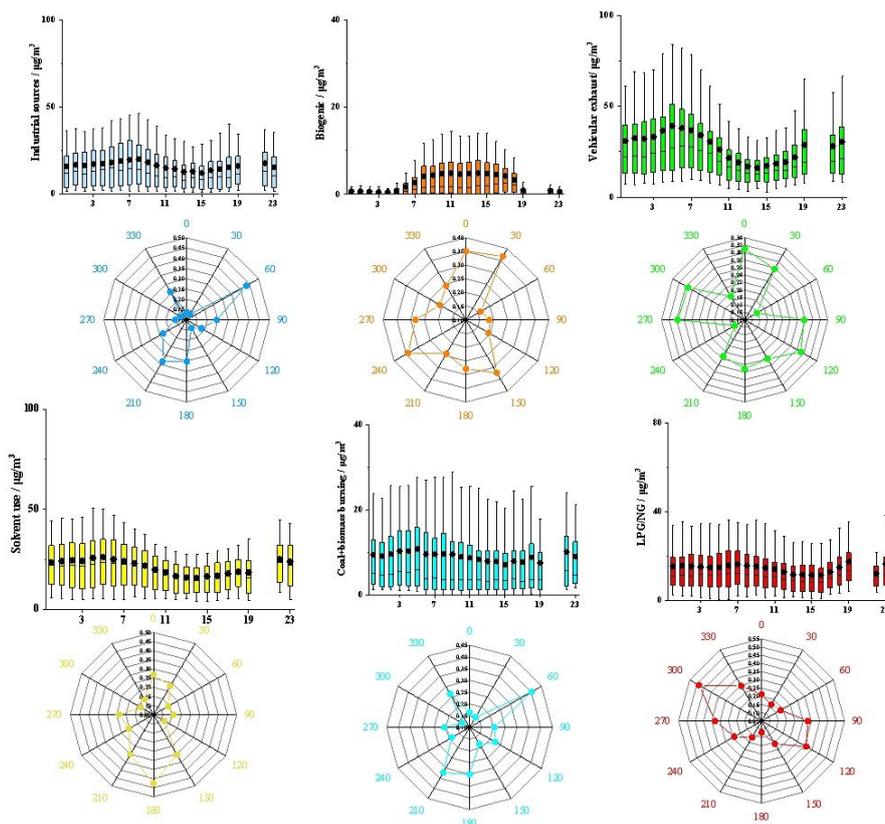
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899   **Fig. 7** Conditional probability function (CPF) plots of local VOC sources in
900   Zhengzhou. The mean (dot), median (horizontal line), 25th and 75th percentiles
901   (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) for
902   the entire study are shown.
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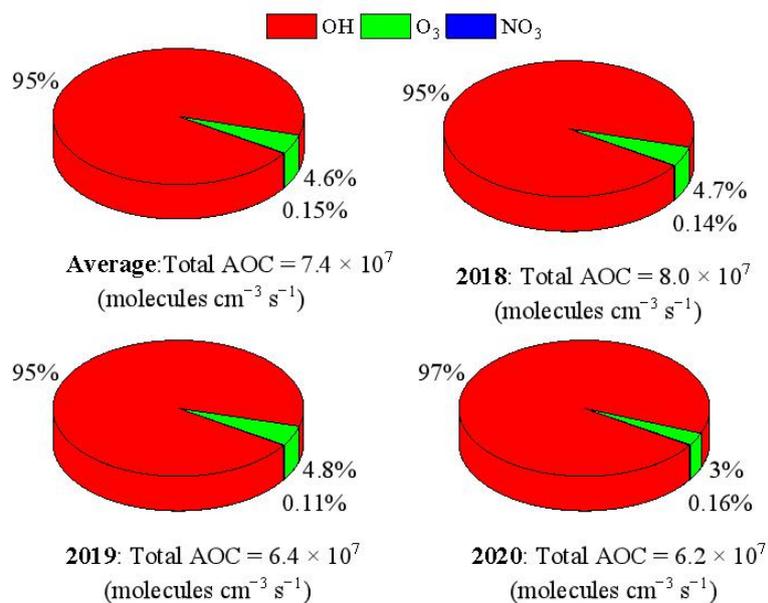
905   **Fig. 8** Comparison of the relative contributions of OH, O$_3$ and NO$_3$ of the AOC in
906   Zhengzhou during the sampling periods.
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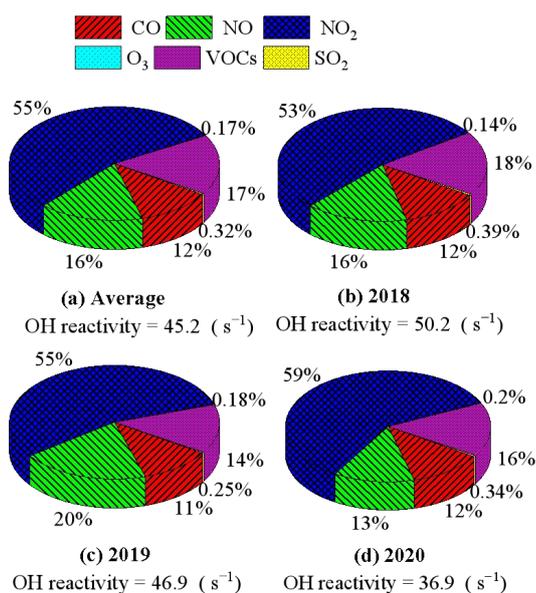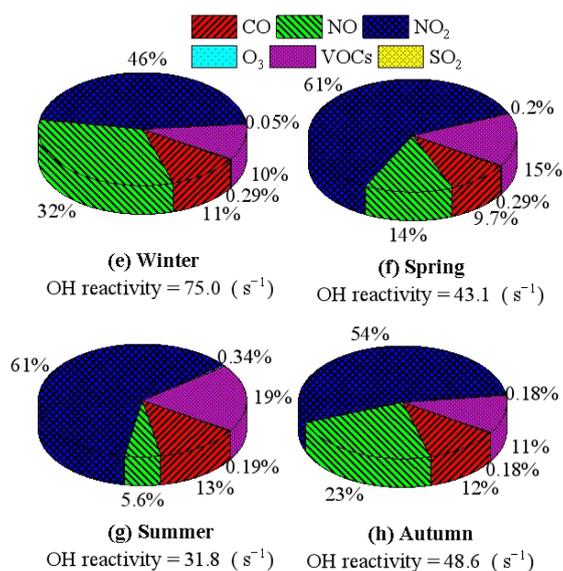
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912   **Fig. 9** Comparison of the relative contributions the OH reactivity in Zhengzhou .
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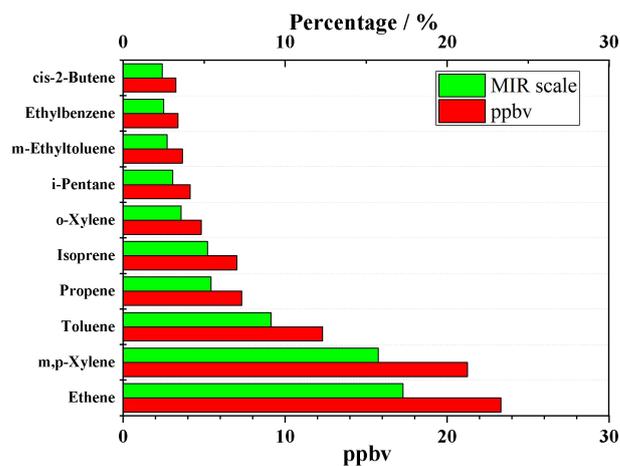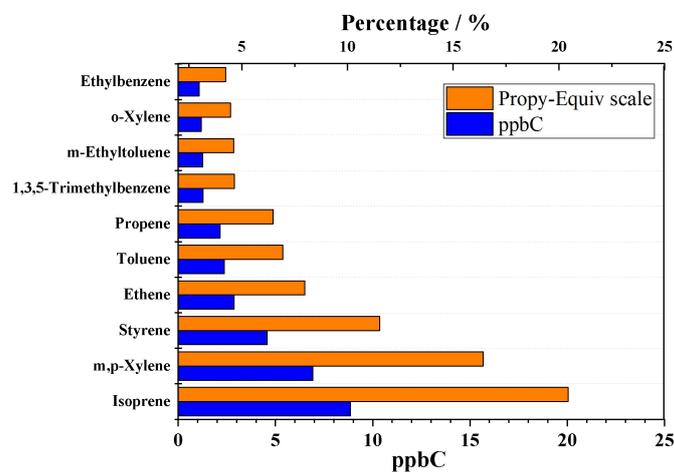
918   **Fig. 10** Top 10 VOCs species that contributed most to the Propy-Equiv and MIR
919   weighted concentrations in Zhengzhou.

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Table list:

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925 **Table 1** Top 20 most abundant VOC species (ppbv) measured in Zhengzhou for the
926 study period 2018-2020.
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928 **Table 2** Comparison of source contributions resolved by PMF models in different
929 cities.
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931 **Table 1** Top 20 most abundant VOC species (ppbv) measured in Zhengzhou for the
932 study period 2018-2020.

Species	2018	Species	2019	Species	2020	Species	Average
Ethane	10±5.6	Ethane	8.7±5.7	Ethane	7.6±3.9	Ethane	8.8±5
Ethene	6±5	Propane	4.5±2.8	Ethene	3.8±2.5	Ethylene	4.7±4
Propane	4.4±2.7	Ethene	3.5±4.3	Propane	3.7±2	Propane	4.2±2.5
Acetylene	4.3±4.3	Acetylene	2.9±4.2	n-Butane	2.1±1.4	Acetylene	2.6±3.3
n-Butane	2.3±1.4	n-Butane	2.4±1.8	i-Pentane	1.4±1.4	n-Butane	2.3±1.7
i-Pentane	2.0±1.7	i-Pentane	2.1±2.0	i-Butane	1.4±0.9	Isopentane	1.9±2
Toluene	1.9±1	Toluene	1.5±1.1	Toluene	1.4±1.1	Toluene	1.6±1.1
n-Pentane	1.3±1.5	i-Butane	1.5±1.1	Benzene	1±0.5	Isobutane	1.3±1
i-Butane	1.2±0.8	Benzene	1.1±0.7	m,p-Xylene	0.9±1.1	n-Pentane	1.2±1.1
Benzene	1.2±0.7	m,p-Xylene	1.1±0.9	Acetylene	0.7±0.8	Benzene	1.1±0.6
m,p-Xylene	1.1±0.6	n-Pentane	1.1±0.9	n-Pentane	0.7±0.9	m,p-Xylene	1±1
Cyclopentane	0.9±1.0	Propene	0.8±1	Propene	0.6±1.2	Propylene	0.7±1.1
Propene	0.8±0.5	3-Methylpentane	0.6±0.4	1-Isoprene	0.4±0.5	Cyclopentane	0.7±1.1
Ethylbenzene	0.7±0.4	n-Hexane	0.6±0.6	Ethylbenzene	0.4±0.4	Isoprene	0.6±0.9
Isoprene	0.6±0.5	Ethylbenzene	0.4±0.3	Styrene	0.2±0.4	Ethyl benzene	0.5±0.4
3-Methylpentane	0.4±0.4	Isoprene	0.4±0.6	o-Xylene	0.2±0.3	3-Methyl pentane	0.4±0.4
o-Xylene	0.4±0.2	Cyclopentane	0.3±0.7	n-Heptane	0.2±0.3	n-Hexane	0.4±0.5
cis-2-Butene	0.4±0.8	o-Xylene	0.3±0.2	Cyclopentane	0.2±0.5	Styrene	0.3±0.3
Styrene	0.3±0.3	2-Methylpentane	0.2±0.3	m-Ethyltoluene	0.2±0.2	o-Xylene	0.3±0.3
n-Hexane	0.3±0.3	1-Butene	0.2±0.3	3-Methylpentane	0.2±0.2	Heptane	0.2±0.3
∑TOP 20 species/∑VOCs	90%		93%		90%		91%

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935 **Table 2** Comparison of source contributions resolved by PMF models in different
936 cities (%).

City	Sampling periods	Solvent use	Industrial sources	Vehicle exhaust	Combustion	LPG/ NG	Biogenic sources
Taiwan[a]	January–December 2016	29	15	18	-	-	4
Wuhan[b]	September 1, 2016 to August 31, 2017		16	24	19	13	2
Shuozhou[c]	March and August, 2014	-	14	21	30	18	-
Ningbo[d]	December 2012, April 2013, July 2013, and October 2013	7	50	16	-	27	-
Beijing[e]	March 2016 to January 2017	16	10	19	-	12	8
This study	January 2018 to December 2020	24	14	31	9	17	4

937 (a:Huang et al., 2019; b:Hui et al., 2018; c: Yan et al., 2017; d: Mo et al., 2017; e: Li et al., 2020c.)

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