

**Characterization of VOCs and their related atmospheric processes in a central China city
during severe pollution periods**

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Abstract

A five-month campaign (May to September 2017) was conducted to investigate volatile organic compounds (VOCs) at four sites for the first time in Zhengzhou City, Henan Province, China, where ozone (O_3) concentration has shown an increasing trend in recent years. Canister samples were taken for fifty-seven VOCs analysis. During the same period, O_3 and its precursor gases were monitored online at four different sites. The results indicated that the average mixing ratio of $\Sigma VOCs$ (28.83 ± 22.05 ppbv) in Zhengzhou was lower than that in the other Chinese megacities, while alkyne was in a higher proportion. The cluster analysis indicating that current from cities south to Henan was cleaner. The abundances, compositions and ratios of typical VOCs showed clear spatial and temporal variations. The VOCs / NO_x ratios indicated that VOCs were more sensitive to the O_3 formation period in Zhengzhou. Furthermore, the source apportionment was conducted with Positive Matrix Factorization (PMF), and it was found that consumption of compressed natural gas (CNG)/liquefied petroleum gas (LPG), the evaporation of gasoline and the exhaust emissions from vehicles were the major sources for ambient VOCs at all four sites.

1. Introduction

Volatile organic compounds (VOCs) are diverse and reactive chemicals. Vehicle exhausts, fuel combustion and evaporation, and solvent usage are the known major anthropogenic sources of VOCs (Zhang et al., 2014; Liu et al., 2017; Sahu et al., 2017). Since VOCs play a crucial role in the formation of ground-level ozone (O_3) pollution, which has troubled many urban cities worldwide with the rapid economic development (Wang et al., 2017c; Nagashima et al., 2017), studies on VOCs are being conducted globally (Wei et al., 2014; Malley et al., 2015; Ou et al., 2015). In China, investigations involving the source apportionment of VOCs, acquirement of emission profiles and interpretation of the seasonal variations were mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and Beijing-Tianjin region (BJT) (An et al., 2014; Wang et al., 2014; Chen et al., 2014; Liu et al., 2016a; Guo et al., 2017), while studies in less developed or developing regions, such as southwestern and northwestern China, where contributions from the burning of

40 biomass with high abundances of toxics and reactive compounds (such as, benzene) are prominent,
41 are very limited. (Li et al., 2014;Li et al., 2017a).

42 Fifty-seven VOCs, including C₂ - C₁₀ alkanes, alkenes, alkynes and aromatics, which greatly
43 contribute to ambient O₃, have been defined and are regularly monitored by Photochemical
44 Assessment Monitoring Stations (PAMS) (Shao et al., 2016;Chen et al., 2010). Due to differences
45 in the structure and reactivity of these compounds, abilities to influence ozone production were
46 varied accordingly, and it is reported that aromatics and alkenes were responsible for most of the
47 weighted reactivity of VOCs (59.4% and 25.8%, respectively) in PRD in China (Ou et al., 2015).
48 Consequently, researchers have deduced that reductions of alkenes and aromatics would be more
49 profit for ozone control (Carter., 1994). In addition, with the changes in energy structure, industrial
50 construction and meteorological conditions (Wang et al., 2015;Shao et al., 2011), major emission
51 sources of VOCs have been changed as well, resulting in varied importance of different sources in
52 ozone formation. For example, in less developed cities, such as Heilongjiang and Anhui, the
53 combustion of biomass had the highest contribution to O₃ formation potential (40% and 36%,
54 respectively) due to high agricultural activities there, while in the developed regions, such as
55 Shanghai, Beijing and Zhejiang, the solvent use has become more important (>20%) (Wu and Xie,
56 2017) than other sources. Identifying major emission sources of VOCs locally would provide
57 scientifically based information for policy-makers to set up strategies to alleviate O₃ pollution.

58 In addition to the factors discussed above, non-linear relationships among the ambient VOCs,
59 nitrogen oxide (NO_x) and O₃ production indicate that the reduction in tropospheric O₃ is complex
60 (Lin et al., 1998;Hidy and Blanchard, 2015;Li et al., 2018). Many modeling and field studies have
61 shown that photochemical production of O₃ in several regions in China, such as Guangzhou,
62 Shanghai and Beijing due to high NO_x, were sensitive to VOCs (Shao et al., 2009;Gao et al.,
63 2017;Ou et al., 2016), and the sensitivity regime was always varied with time and geographical
64 locations (Luecken et al., 2018). The percentage of VOC-limited regime in North China Plain (NCP)
65 has expanded from 4% to 6% during 2005-2013, because of the rapid increasing emissions of NO_x
66 (Jin and Holloway, 2015).

67

Zhengzhou City is an important developing city in the mid-west of the Huanghe-Huaihe river flood plain in China. As the capital city of Henan Province, it is densely populated with more than seven million residents (in 2010) (Geng et al., 2013). With the rapid growth of industrial activities, as well as increased vehicle emissions and fuel combustion, air quality in Zhengzhou has notoriously deteriorated, exceeding the allowable limits by 65% of days (air quality index, AQI>100) in a year set by Air Quality Guideline in 2013. Particularly, O₃ was the major pollutant (Shen et al., 2017; Gong et al., 2017) in summer and over 50% of the days in a year, the mixing ratio of O₃ exceeded the Grade I standard of daily maximum average 8-hour (DMA8) (100 µg m⁻³) in Henan. As one of the major precursors of O₃, the study on VOCs is of significance for Zhengzhou, since no related researches are published in peer-reviewed literature. In this work, a comprehensive sampling campaign aiming at VOCs has been conducted at four monitoring stations during the time period of May - September 2017. The spatial and temporal variations in VOCs in Zhengzhou were determined. The contributions of major emission sources were quantified, and the relationship among O₃-VOCs-NO_x was discussed in details. The results and implications from this study can provide useful guidance for policy-makers to alleviate ozone pollution in Zhengzhou, China.

2. Observation and Methodology

2.1 Sampling site

Based upon the density of population, industrial facilities, and the prevailing winds, four sites have been selected for sample collection: Jingkai community (JK; 113.73°E, 34.72°N), municipal environmental monitoring station (MEM; 113.61°E, 34.75°N), Yinhang school (YH; 113.68°E, 34.80°N) and Gongshui company (GS; 113.57°E, 34.81°N), which are located at the southeastern, southwestern, northeastern and northwestern of Zhengzhou, respectively (Fig. 1). There is a main airport highway and heavy-traffic ring roads approximately 500 m west of JK. Furthermore, the site is at a distance of 2 km from an industrial area, which involves packaging and printing plants, and material distribution factories. It is noteworthy that there were three coal-fired power plants in the urban area of Zhengzhou city. One of the power plants with the highest production was 1.6 km northwest of MEM. Both the MEM and YH include a mix of commercial and condensed residential

areas, whereas the apartments around YH are more aged. The GS site is surrounded by several manufacturing plants, including pharmaceuticals, materials, foods and machineries.

Ten sampling days with the rainfall record (*ca.* 0 mm) were chosen in every month during the period of May - September, 2017 consequently, to represent a typical air quality conditions in a month. The whole air samples were collected in one minute using 3.2 L stainless-steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA), which were pre-cleaned with high purity nitrogen and pressurized to 20 psi. Two samples, one collected at 07:00 with increasing of human activities and another one collected at 14:00 with well-mixed of ambient air, were obtained on each sampling day. There were a total of 400 valid samples collected in this study. The chemical analysis was accomplished within two weeks after the collection of samples. Real-time data for trace gases, including SO₂, CO, NO₂ and O₃, and synchronous meteorological data, such as temperature (T), relative humidity (RH), wind direction (WD) and wind speed (WS), were recorded at each air monitoring station.

2.2 Chemical Analysis

In this study, the measurement of VOCs was based on Compendium Method TO-15, which was established by U.S. EPA. Air in the canister was concentrated using liquid-nitrogen at -160 °C in a cryogenic pre-concentrator (7100A, Entech Instrument, Inc.). Both the CO₂ and H₂O were removed from the transfer line. The air was then thermally desorbed at 120 °C and transferred for analysis to a gas chromatograph(GC, 7890A, Agilent Technologies, Santa Clara, CA, USA) coupled with dual detectors, i.e. a mass spectrometric detector (MSD) and a flame ionization detector (FID) (5977E, Agilent Technology). Dual columns were applied for the simultaneous analysis of C₂ - C₁₁ hydrocarbons. A PLOT column (15 m, internal diameter of 0.32 mm and film thickness of 3.0 µm) was connected to the FID for detection of C₂ - C₅ NMHCs, whereas C₅ - C₁₀ NMHCs, oxygenated VOCs (OVOCs) and halocarbons were separated using a DB-624 column (30 m×0.25 mm inner diameter × 3.0 µm film thickness), which was connected to the MSD. Target compounds were identified with retention time and mass spectra, and quantified with multi-point calibration curve in this study. The standard gas named with PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to build calibration curves, which containing 57 VOCs, including 28 alkanes, 11

124 alkenes, acetylene and 17 aromatics. Detailed information on the 57 hydrocarbons involved in this
125 study and their corresponding linearity of calibration (R^2), measurement relative standard deviation
126 (RSD), method detection limit (MDL), maximum increment reactivity (MIR, carter, 2010) are
127 presented in Table S1.

128 2.3 Positive matrix factorization (PMF)

129 U.S. EPA PMF 5.0 was used for source apportionment (Lau et al., 2010;Abeleira et al.,
130 2017;Xue et al., 2017). PMF is a receptor model can shed lights on distribution of major sources,
131 with the assumption that no chemical loss would happen during the transportation from emission
132 sources to the measurement site, although which was violated with the fact that compounds usually
133 endure consumptions due to reactions with oxidants (such as O_3 , NO_3 etc.) in ambient air. The
134 rational and mathematical details for PMF were presented in supporting information.

135 With principles such as, (1) species with mixing ratios usually below MDL were eliminated; (2)
136 except for the source markers, species with high reactivity should be excluded (Shao et al.,
137 2016;Guo et al., 2011); 28 VOC species and NO_2 were chosen for the source analysis.

138 In this study, PMF was performed with fifty base runs for each site, results with the minimum
139 Q value were considered as optimum solutions. In Table S2 the r^2 between observed values and
140 predicted values of 28 VOCs and NO_2 are presented for the four sites, the r^2 for most species (>80%)
141 were higher than 0.6, compounds with $r^2 < 0.6$ were down weighted when determine factor sources.

142 During PMF analysis, bootstrap method was used to evaluate stability and uncertainty of the
143 base run solution, setting the minimum correlation R-value at 0.6, 100 bootstrap runs were
144 performed, and the results were showing in Table S3, and acceptable results (>80%) were gained
145 for most factors.

146 Three to nine factors were selected to initiate running of PMF, the $Q/Q(\text{exp})$ for every site at
147 fixed factor size were presented in Table S4. With the increase of factor number, the ratios $Q/Q(\text{exp})$
148 were declined due to additional factors. When the factor size changing from 3 to 4, 4 to 5, and 5 to
149 6, the decrement of $Q/Q(\text{exp})$ were larger (about 12-23%), while the change was lower than 10%
150 after factors increased to 7, combined with the field conditions, seven factors were defined at MEM,

YH, and GS, and eight factors were defined at JK (Fig.2). the weight percentage of each factor at the four sites were presented in Fig.3

3 Results and discussions

3.1 Meteorological variations and Mixing ratios

Meteorological conditions are important factors that impact both the compositions and levels of VOCs. During the sampling period, the T(RH) was varied from 15°C(15%) to 38°C(100%) (Fig.S1), the dominant wind was northwestern and southeastern (Fig. 4). The air clusters, analyzed by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, have some differences in each month (Fig. 5). In May, clusters arriving at Zhengzhou demonstrated longer paths, and included six clusters in total, while in June, the length of clusters were shorter. However, the concentration levels and compositions of VOCs were similar at the two months. In May, the largest cluster (27.2%) was passed over from the origin city, Yinchuan, a central city in northwest China, crossing several non-capital cities (such as, Yanan, Yuncheng and Luoyang) in Shanxi and Sichuan provinces. Such a long-range transport of pollutants might have less impact on the air quality of Zhengzhou, as a comparable level and similar compositions of VOCs were obtained during the period of May - June. In the months of June, August and September, approximately half of the air trajectories originated from the areas of Henan province, indicating the air pollutants in Zhengzhou was impacted by local factors at most time.

In Table 1 the total concentrations of VOCs (Σ_{VOCs}) are presented. The Σ_{VOCs} were different for all the months at all the sites and the site having the highest Σ_{VOCs} was not the same in each month. In May 2017, the highest Σ_{VOCs} was reported at JK (37.65 ± 22.58 ppbv), followed by GS (31.73 ± 18.70 ppbv), YH (30.05 ± 16.43 ppbv) and MEM (29.05 ± 15.34 ppbv), while the Σ_{VOCs} values for the month of June, July, August and September were found to be in the order of: GS>JK>MEM>YH, MEM>GS>JK>YH, YH>MEM>JK>GS, and MEM> YH > GS >JK, respectively. This can be attributed to numerous factors that will be explored later in the paper. Besides the emission sources (to be discussed in Section 3.2), the impacts controlled by meteorological conditions should not be ignored as well. For instance, the prevailing wind in May

was northwestern at GS and YH, while the southwestern wind was dominant at JK (Fig 6). The transport of air pollutants from urban center and industrial plants should have resulted in the highest level of Σ_{VOCs} at JK. In June 2017, the prevailing wind was southeastern at MEM, YH and GS (Fig. 4). The average wind speed at GS ($0.74 \pm 0.33 \text{ m s}^{-1}$) was lower than that at MEM ($1.84 \pm 0.94 \text{ m s}^{-1}$) and YH ($0.97 \pm 0.36 \text{ m s}^{-1}$) (Table 2), indicating poor dispersion conditions at GS. The air pollutants emitted from MEM and YH were more liable accumulated at GS, resulting in a higher level of Σ_{VOCs} at GS in June. It should also be noted that, when Σ_{VOCs} at JK was higher than that of GS, the levels at YH were higher than those of MEM, and vice versa. Except for the discriminations between the pollution sources at every site, the above phenomenon might be a result of the topography with a gradual increasing elevation from east to west in Zhengzhou (Mu et al, 2016).

Due to the variation of the planet boundary layer (PBL) height, solar radiation and emission sources etc. day and night, the concentrations of VOCs displayed obvious differences between morning and afternoon time (07:00LT and 14:00LT in this study). Compared with morning period, the aromatic compounds showed lower compositions around 14:00 LT (Fig. 7), because of the increased planet boundary layer and the active photochemical reactions, while alkenes always peaked in afternoon time. According to the dataset, the increases in alkene compositions (about 4.3% uplift) were mainly due to higher contributions of isoprene (about 1.4% at morning and 7.6% in the afternoon), which was mainly emitted from biogenic sources and increased exponentially with temperature (Jiang et al., 2018). In addition, with the heavier impact from biogenic source (10.03%) in JK (Fig.3), isoprene's contribution to Σ_{VOCs} value at JK at was 12% at 14:00 LT (Fig.7), much higher than those at three other sites (range from 4.02% to 7.92%).

The average Σ_{VOCs} values in Zhengzhou ($28.83 \pm 22.05 \text{ ppbv}$) were significantly lower than those in Beijing (65.55 ppbv), Hangzhou (55.9 ppbv), Guangzhou (47.3 ppbv) and Nanjing (43.5 ppbv), and higher than that in Wuhan ($23.3 \pm 0.5 \text{ ppbv}$) (Table 3). Factors, including population density, industrial activity, fuel composition, local stringent regulations for environmental protection, terrain, and weather etc. may be the reason for the discrimination of VOCs concentrations in those cities. With regard to the weight percentage of major groups (Table 3), the

composition of alkanes was the largest in all cities because of their long-lives and widespread sources (Fig. 7), while the composition of aromatics was lower than alkenes in these cities except for Guangzhou. It is well known that aromatics mainly originate from solvent usage and vehicle exhaust. The large amount of shoemaking and shipbuilding industries involving large amounts of solvent usage may be the main reason for the higher composition of aromatics in Guangzhou. In comparison with other four cities, the composition of aromatics in Zhengzhou was the lowest probably due to its less manufacturers involved in solvent usage than in Guangzhou, Hangzhou and Nanjing, and less vehicles than in Beijing. Alkyne contributes least to VOCs in cities listed in Table 3, with higher level observed in Zhengzhou (rank second after Hangzhou). Alkyne typically originates from combustion sources. Zhu et al. (2016) observed that the composition of alkyne in the biomass-burning period could be double during the non-biomass burning period. As Henan is the largest agricultural province in China and the sampling duration covered the crop harvest season, the residents often used crop residues as the biofuel for their subsistence and a higher alkyne composition in Zhengzhou was expected.

3.2 Temporal variations

The time series of mixing ratios of NO_x, O₃ and Σ VOCs at every site are shown in Fig. 8. The results showed a distinctive temporal characteristic where lower levels of SO₂, CO, NO_x, O₃ and Σ VOCs were observed in July and August (mid-summer) (Table S5). These results were similar to those obtained for other urban areas (Li and Wang, 2012; Cheng et al., 1997; Na et al., 2001). Changes in PBL height, human activities, and abundance of hydroxyl radicals (\bullet OH) were the potential causes for the phenomenon. Pal et al. (2012) reported that the PBL height was positively correlated with temperature. The occurrences of precipitation and raining were also frequent in most areas of China during summer, resulting in decreasing background level of air pollutants. Additionally, a series of effective local policies, such as prohibition of painting and coating in open air and limitations on fuel supply between 10:00 -17:00 LT during hot summer days assisted in suppressing the emissions of VOCs. Meanwhile, many organizations, such as schools, institutes and scattered private workshops, were closed due to summer vacations. Some large-scale industries also stopped manufacturing processes for two weeks during this period. Consequently, the

anthropogenic emissions were reduced, which in turn resulted in a decrease in VOCs, SO₂, and NO_x emissions. The reduction of precursor levels and unfavorable photochemical conditions (such as, higher RH) resulted in the lower O₃ levels in July and August.

Beside local emissions, the long-range air mass also had some impacts on relatively lower level of Σ VOCs in July. As illustrated in Fig. 5, different from other months, the air current originated with the largest portion (*ca.* 88.68%) of clusters from Hubei province, where the average Σ VOCs observed in its capital city (23.3 ± 0.6 ppbv) (Lyu et al., 2016) was lower than that in Zhengzhou (29.18 ± 23.08 ppbv). In combination with the lower weight percentage of aromatics ($10.30 \pm 4.23\%$), which have high photochemical reactivity, and the lowest T/B ratio (1.15 ± 0.99) around this period, it is possible that the cleaner air mass clusters originating from Hubei also contributed to the reduction of Σ VOCs in July.

As demonstrated in Fig. 8, the observed Σ VOCs values at 07:00 LT were often higher than those at 14:00 LT. The accumulation of pollutants during night-time and the temperature inversion in the morning were the most reasonable explanations for this phenomenon. Stronger photochemical reaction during noon-time led to the reduction in atmospheric VOCs. It should be noted that pronounced Σ VOCs were occasionally observed at MEM and GS (Fig. 9), which were potentially ascribed to sharp changes in local emissions and meteorological conditions. At MEM, the distinctive increment was always accompanied by obvious increases of alkanes or aromatics (Fig. 9). Since the T and RH were often consistent during the sampling period, the direct gas evaporations should be constant. Therefore, the simultaneous increased concentrations of SO₂, CO and NO_x could illustrate the potential impacts from combustion sources, such as emissions from nearby thermal power plant. At GS, the increase of Σ VOCs in June was usually with extremely high levels of aromatics, due to the disturbance from solvent use for building renovation during this period, and the abnormal high levels of Σ VOCs in other months were related to the rising concentrations of C₃-C₄ alkanes, which mainly originated from consumptions of compressed natural gas (CNG) or LPG (Huang et al., 2015b), indicating the possible impact from a gas-fueled power plants located about 1 km southwest of the site (about 18% was western wind at GS during May to September).

262 It is of interest to note that on the morning of 5th September, acetylene was found in extremely
263 high concentrations (14.65 - 39.42 ppbv). Its mixing ratio in most of the urban areas was <10 ppbv
264 (Louie et al., 2013; Duan et al., 2008; Guo et al., 2012). It was learnt that the 5th September is a
265 festival day for the people, who worship their ancestors. A large number of incenses and offerings,
266 made up of wood and paper, were burnt during the festival, resulting in an increase in the mixing
267 ratio of acetylene (Zhu et al, 2016) all over the Zhengzhou city.

268 3.3 Spatial variations

269 C₂ - C₅ alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs
270 detected at all sites (Fig.10), and the mixing ratios of toluene varied within a wide range at each site,
271 because of its universal emission sources (Wang et al., 2014; Barletta et al., 2005), among which,
272 vehicle exhaust emissions and solvent usage are the major contributors. These chemicals
273 contributed >60% for Σ VOCs at each site, in line with the source apportionment results (Fig. 3),
274 CNG/LPG usage, gasoline evaporation and vehicle exhaust had considerable portions and were the
275 important sources for ambient VOCs at every site.

276 Among the four major organic classes, alkane was the most abundant group as a result of busy
277 traffic in urban city and its longevity (Fig.7), and accounted for 52.85%, 62.52%, 53.38%, 53.39%
278 of the total Σ VOCs values at JK, MEM, GS, and YH, respectively. The highest composition of alkane
279 was observed at MEM due to the stronger contributions of ethane, iso-pentane, cyclohexane,
280 methylcyclohexane, 2-methylhexane and 3-methylhexane (Fig. S3), which were identified as the
281 components heavily impacted by petrochemical industries (Jobson et al., 2004; Mo et al., 2015). In
282 accordance with the higher contribution of petrochemical source (11.56%) at MEM (Fig. 3).

283 Average Σ VOCs were slightly higher at industrially impacted sites of GS (31.66±28.73 ppbv) and
284 JK (28.63±22.04 ppbv) than those at MEM and YH (Fig.11). Additionally, the air pollutants related
285 to the combustion process, such as SO₂ and CO, were more abundant, though marginal, in western
286 area of Zhengzhou (GS and MEM) (Fig.11), fitting to the higher contribution of coal combustion at
287 GS and MEM (13.50% and 17.84% respectively) according to PMF results (Fig.3). With high
288 VOCs and sufficient NO_x, the highest average mixing ratio of O₃ was observed at GS, followed by

YH site even with the lowest VOCs and NO_x, indicating there are many other factors, in addition to the absolute concentrations of VOCs and NO_x, which contribute to ozone formation at YH.

In June, the O₃ concentration often exceeded the national standard level of 80 ppbv, causing severe air pollution during this period. The average mixing ratio of O₃ during daytime (07:00-18:00 LT) in June, 2017 at JK, MEM, YH, and GS were 74.87 ± 39.55 ppbv, 73.50 ± 40.59 ppbv, 73.81 ± 35.69 ppbv, and 87.99 ± 46.11 ppbv, respectively (Table 4). The higher level of O₃ at GS is accompanied with a higher Σ VOCs (39.29 ± 25.37 ppbv). The weight percentage of aromatics ($15.62 \pm 12.06\%$) with high reactivity at GS was higher than those at other sites as well, indicating the painting and other renovation activities at GS in June may be an important factor for its high ozone level. Even though both the Σ VOCs and specifically O₃ formation potential compounds (such as, alkenes and aromatics) at MEM were slightly higher than those at YH (Table 4), the O₃ concentration at MEM was not higher than YH, which could be attributed to other critical precursors, such as NO_x. NO at MEM (7.72 ppbv) was significantly higher than that at YH (2.57 ppbv) during daytime, indicating that the titration reaction between O₃ and NO was more efficient at MEM.

It is well known that many O₃ episodes were attributable not only to local sources but also to regional transports. For example, Streets et al. (2007) reported that during continuous southern wind, the ozone level in Beijing was 20-30% contributed by its neighboring city Hebei. During this study, a typical regional ozone pollution was happened on August 10th at YH (Fig.8). On that day, the ratios of Σ VOCs/NO_x at the four sites were all less than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that VOCs are the critical contributors to the formation of O₃ in Zhengzhou. The reductions in Σ VOCs in the afternoons (around 14:00 LT) compared to mornings (around 07:00 LT) may have been caused from the uptake by O₃ formation, while the reduction of Σ VOCs and active compounds (i.e., aromatic+alkene) at 14:00 relative to 07:00, determined as 35% and 56% respectively, were the least at YH among the four sites (Fig. S4). On the other hand, based on the dispersion of wind direction, between 08:00 - 15:00 LT on August 10th, YH was at the downwind position to the other three sites (Fig. S4). All of this confirmed that the abnormally high O₃ at YH was caused by the transport of air pollutants from other sites on that day.

3.4 VOCs/NO_x ratio

The VOCs/NO_x ratio is usually used to establish whether a region is VOCs or NO_x limited in ozone formation. In this study, the mean level of VOCs /NO_x (ppbC/ppbv) were below 5 at all four sites (Fig.12), and 75% data points were less than 6 at each site, indicating that the ozone formation were controlled by VOCs in Zhengzhou, and the reductions on the emissions of VOCs will be benefit for ozone alleviation.

The specific data distribution of VOCs /NO_x showed some differences in the four sites (Fig. 12), with the lowest value presented at MEM (about 3.8), and the highest value observed at JK (about 4.7), demonstrating that due to the impact of thermal-power plant, the production of ozone at MEM was more sensitive to VOCs than JK. Meanwhile, about 14% of the VOCs /NO_x ratios (>8.0) were located in the NO_x-limited area at JK, which may be a result of its higher VOCs or lower NO_x emissions than other sites. Both the statistical data and the mixing ratios showed higher levels of VOCs (with lower NO_x) at GS, where only 4% of the ratios larger than 8 has been observed, indicating that there must be some other factors (unknown in this study) impact the variation of ozone formation regimes.

As to the daily variation of VOCs /NO_x ratios (Fig. 12), higher values at 14:00 relative to 07:00 were observed at the four sites, which may be correlated with less vehicle emissions or more consumption path of NO_x at noon time. The increment of VOCs /NO_x at 14:00 relative to 07:00 was more obvious at JK and GS, showing more emission sources of VOCs at these two sites at daytime, and resulting the ozone formation system at JK and GS shifting to the transition area in the afternoon.

Researches have shown that ozone formation depends not only on its precursors (mainly VOCs and NO_x), but also has VOCs /NO_x ratios (Pollack et al., 2013). In our research, the mixing ratio of O₃ at 14:00 LT presented a small positive trend ($p < 0.05$) with the uplift of VOCs /NO_x at JK (Fig. 13), which was similar to the results observed at Shanghai (Gao et al., 2017), where the O₃ formation was more sensitive to NO_x concentration under high O₃ levels. This may be a result of

the increased ozone production efficiency at high VOCs /NO_x. There were no discernible trends at other sites, possibly due to the counteraction imposed by other uncertain factors.

3.5 Ratios of specific compounds

Ratios of specific VOCs are useful indicators to identify the emission sources (Raysoni et al., 2017;Liu et al., 2015;Ho et al., 2009). In order to characterize the differences in the contribution of various sources at each site, the toluene/benzene (T/B) and i-pentane/n-pentane ratios are discussed.

The ratio between i-pentane and n-pentane can be used to differentiate potential sources such as consumption of natural gas, vehicle emissions and fuel evaporations etc. It is claimed that in areas heavily impacted by natural gas drilling, the ratio was lied within the range of 0.82 - 0.89 (Gilman et al., 2013;Abeleira et al., 2017) and higher values were often reported for automobiles, such as 2.2 - 3.8 for vehicle emissions, 1.8 - 4.6 for fuel evaporation, and 1.5 - 3.0 for gasoline (Russo et al., 2010;McGaughey et al., 2004;Jobson et al., 2004;Wang et al., 2013b), low values within the range of 0.56 - 0.80 were found for coal combustion .

In this study, i-pentane and n-pentane were highly correlated ($R^2=0.78 - 0.89$) throughout the whole sampling campaign (Fig. 14), indicating similar sources for these two compounds. The highest ratio of i/n-pentane was found at JK (2.73), which was comparable to the value of 2.93 reported in a Pearl River Tunnel (Liu et al., 2008), thus indicating strong impacts from traffic-related sources (more than 29% by PMF). The average ratio at MEM was 2.02, which was inconsistent with the characteristics of coal combustion. Yan et al. (2017) reported that the ratio for areas influenced by several coal-fired thermal power plants was approximately 0.55. The bias could be explained by factors, such as production scales, fuel compositions, sampling time and terrain etc. Additionally, it is remarkable that MEM was surrounded by a main road with four traffic lanes. The distance between the nearest traffic light and the sampling site was just 200 m. Frequent idling may cover up the contribution from coal combustion, thus largely showing the effect of traffic emissions, in accordance with the PMF results that more than 18.47% of VOCs were related with mobile sources and only17.84% related with coal combustion. The average ratio at GS (1.85) was close to

that at YH (1.68) due to the comparable contribution from vehicle exhaust (29.24% and 26.14%, respectively).

T/B is an efficient tool to differentiate between pollution sources, both the tunnel studies and roadside researches indicated that T/B ratio varied within the range of 1 - 2 when the atmosphere was heavily impacted by vehicle emissions (Gentner et al., 2013; Tang et al., 2007; Huang et al., 2015b; Wang et al., 2002), and when the ratio was less than 0.6, it may be due to other sources, such as coal combustion and biomass burning (Tsai et al., 2003; Akagi et al., 2011). The industrial activity would become more important when the value of T/B ratio is higher than 3 (Zhang et al., 2015). In addition, the atmospheric lifetimes of toluene and benzene are different, it was reported that when the $\bullet\text{OH}$ concentration was assumed to be 10^6 rad cm^{-3} (Monod et al., 2001), the lifetime for toluene and benzene was 1.9 days and 9.4 days, respectively, which maybe one of factors for the lower T/B ratios at 14:00 LT than those at 07:00 LT, and higher T/B ratios in September.

In this study, the R^2 value for the correlation between benzene and toluene was better in May (0.73 - 0.84) than during other months for all sites (Fig. 15), indicating the source of benzene and toluene in May was more similar, and the average ratio in May varied within the range of 1.81 - 3.36 for all four sites, suggesting that evident impacts were observed from vehicle emissions on the VOCs during this period.

For each site, the T/B ratio was scattered in different ranges, suggesting spatio-temporally varied emission sources (Fig. 15 and Fig.S5). Except for September, the average T/B ratio at JK lied within the range of 1.47 - 2.72, testified the heavily impact from vehicle emissions sorted by PMF, where traffic related source accounted for more than 29% emissions (Fig.3). Meanwhile, many automotive-related workshops and printing shops were located approximately 2 km southwest of JK, resulting in the higher contributions from solvent use (12.32%, weighted on the same 7 factors), for less interruption from photochemical reaction, the impact from industrial clusters were rising, and generating higher T/B value (3.89) in September at JK. The T/B ratio at MEM was on the low side during the period of May - August (0.96 - 1.68), highlighting the impact of coal-fired thermal power plant. As to GS, the average T/B ratio varied in the range of 0.44-1.17 from June to August and exhibited clear characteristics related to the combustion of coal/biomass.

On the one hand, GS was located on the edge of Zhengzhou, and during the harvesting season the impacts from biomass burning would be heavier than other areas. On the other hand, one coal fired power plant was located about 5 km southeast of GS, and with the prevalent wind direction of southeastern from June to August, the air pollutants emitted from the power plant could be easily transported to this region.

Overall, based on the iso-pentane/i-pentane, T/B ratios and PMF results, the traffic emissions at JK and combustion sources (related to coal or biomass) at MEM and GS, would account for more contributions to VOCs, while there were no consistent results observed for YH due to the wide span of T/B ratio (1.07 - 5.38).

The ratio between i-pentane and n-pentane is also useful in differentiating between potential sources. It is claimed that in areas heavily impacted by natural gas drilling, the ratio was lied within the range of 0.82 - 0.89 (Gilman et al., 2013;Abeleira et al., 2017) and higher values were often reported for automobiles, such as 2.2 - 3.8 for vehicle emissions, 1.8 - 4.6 for fuel evaporation, and 1.5 - 3.0 for gasoline (Russo et al., 2010;McGaughey et al., 2004;Jobson et al., 2004;Wang et al., 2013b), low values within the range of 0.56 - 0.80 were found for coal combustion . In this study, i-pentane and n-pentane were highly correlated ($R^2=0.78 - 0.89$) throughout the whole sampling campaign (Fig. 15), indicating similar sources for these two compounds. The highest ratio of i/n-pentane was found at JK (2.73), which was comparable to the value of 2.93 reported in a Pearl River Tunnel (Liu et al., 2008), thus indicating strong impacts from traffic-related sources (more than 29%). The average ratio at MEM was 2.02, which was inconsistent with the characteristics of coal combustion. Yan et al. (2017) reported that the ratio for areas influenced by several coal-fired thermal power plants was approximately 0.55. The bias could be explained by factors, such as production scales, fuel compositions, sampling time and terrain etc. Additionally, it is remarkable that MEM was surrounded by a main road with four traffic lanes. The distance between the nearest traffic light and the sampling site was just 200 m. Frequent idling may cover up the contribution from coal combustion, thus largely showing the effect of traffic emissions, in accordance with the PMF results that more than 18.47% of VOCs were related with mobile sources and only 17.84% related with coal combustion. The average ratio at GS (1.85) was close to that at YH (1.68) due to

the comparable contribution from vehicle exhaust (29.24% and 26.14%, respectively). Consistent with the verdict gained from T/B ratios, the value of iso-pentane/i-pentane also showed that the vehicle emissions were an important source for VOCs in Zhengzhou city.

3.6 Relative reactivity of VOCs

The reactivity of individual species was different, and the various mixtures of VOCs would result in competition between different species, leading to different reaction paths and relative ozone formation yields. Ozone formation potential (OFP) is a useful tool to estimate maximum O₃ productions of each compound under optimum conditions, from which the vital species in ozone formation could be identified (Huang et al., 2017). The calculation of OFP is based on mixing ratios and maximum incremental reactivity (MIR) of individual compound, which are expressed in Eq. (4).

$$\text{OFP} = C_i \times \text{MIR} \quad (4)$$

where C_i represents the concentration level of i^{th} species, while MIR is a constant taken from Carter (2010) (Table S1).

In Zhengzhou city, it was alkenes contribute most ($55.91 \pm 14.17\%$) to the sum of OFP, of which ethylene taken a large portion. This is different from the results estimated based on emission inventories by Wu and Xie (2017), where the largest contributor of total OFP in North China Plain (NCP), YRD and PRD was aromatics, hinting at the relatively lower surface coating industry in Zhengzhou

As to individual species, the 10 most contributors in OFP included ethylene, isoprene, m,p-xylene, toluene, propylene, acetylene, n-butane, i-pentane and propane, together their contributions to the sum of OFP was lied within the range of 74.64 - 79.90% (Table 5), with 61.30-76.46% of total VOCs weighted in concentration, highlighting the importance of reduction on emissions of these VOCs. Additionally, it is worth noting that, the percentage of acetylene ($4.51 \pm 0.34\%$) weighted in OFP was higher than many other areas in China, including Guangzhou (2.20%) and YRD (2.37%) (Li and Wang, 2012; Wu and Xie, 2017), demonstrating that it is

necessary to conduct emission controls on sources related to combustion (such as, vehicle emissions and biofuel burning) in Zhengzhou city .

Zhengzhou was suffered from the severest O₃ pollution in June, 2017. The relationships between OFP of each organic group, ΣVOCs , and the concentrations of NO_x and O₃, as well as the corresponding meteorological conditions, are shown in Fig. S6. At every site at 07:00 LT, WS was generally lower than that at 14:00 LT, providing an available conditions for local ozone propagation . With the lower RH, higher T and OFP (88.13 ± 30.32 ppbv) values, the O₃ level at YH was unexpectedly lower than that at MEM on sunny days, keeping in mind that the OFP was estimated with the assumption of reactions were proceed under optimum conditions, the above phenomenon reflected the unsatisfied ozone formation conditions at YH. The total OFP was highest at JK in June, while the highest O₃ levels was observed at GS, during this period GS was downwind of other sites with lowest WS(0.74 ± 0.33 m s⁻¹) , and the concentration level of O₃ usually increased with wind speed (Fig.S7), particularly when the eastern wind was dominant, illustrating the disturbance from long-distance sources in urban center.

4. Conclusions

In this study, 57 VOCs were collected at four different sites in Zhengzhou, Henan (China) for the first time. The air pollutions in Zhengzhou were mostly impacted by local factors according to the cluster analysis, and air clusters from Hubei occasionally arrived at Zhengzhou was cleaner. In comparison to other Chinese cities, the weighted percentage of aromatics was lower, but higher alkyne was observed in Zhengzhou city. Due to less anthropogenic emissions and more favorable dispersion conditions, most of the air pollutants had the lowest levels in the mid-summer month of July. C₂ - C₅ alkanes, acetylene, ethylene, toluene and benzene were the most abundant VOCs in the region, indicating the general consistency of pollution sources, mainly CNG/LPG usage, gasoline evaporation and vehicle exhaust according to the source apportionment results. On the basis of monthly average, the maximum ΣVOCs was observed at GS, because of the occasional impact from the nearby gas fueled plant. Approximately 75% of VOCs/NO_x ratios were below 6 at each site, indicating that the O₃ formation was driven by VOCs regionally. Thus, this potentially demonstrates that the O₃ formation was more sensitive to the abundance of VOCs in Zhengzhou.

479 Different from other megacities, alkenes were the biggest contributors to OFP, and acetylene was
480 particularly critical at each site, illustrating the necessary to conduct emission controls on
481 combustion sources, mainly vehicle emissions, coal combustion and biofuel burning, in Zhengzhou
482 city. This study provides the first-hand information on the characteristics of VOCs and assists in
483 overcoming the O₃ pollution issue in Zhengzhou city, China.

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489 **Table & Figure**

490 Table1. Concentrations of ΣVOCs (ppbv) at every site during the sampling period

	JK		MEM		GS		YH	
	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.
May.2017	37.65	22.58	29.30	15.34	31.73	18.70	30.05	16.43
June.2017	34.02	19.89	30.28	12.77	39.29	25.37	28.33	11.94
July.2017	16.01	6.13	20.74	12.66	19.60	13.94	15.95	7.54
Aug.2017	21.54	15.29	24.37	20.79	20.49	15.67	26.03	17.01
Sept.2017	26.20	16.22	34.15	23.85	30.36	19.76	32.56	19.76

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492 Table2. Wind speed ($\text{m}\cdot\text{s}^{-1}$) at every site during the sampling period

	JK	MEM	YH	GS
May	1.34±0.65	1.86±1.19	1.27±0.66	0.97±0.49
June	1.07±0.48	1.86±0.94	0.97±0.36	0.74±0.33
July	1.48±0.59	2.62±1.19	1.15±0.45	0.90±0.32
August	1.06±0.48	1.86±0.94	0.95±0.39	0.76±0.35
September	0.80±0.38	1.24±0.80	0.82±0.43	0.62±0.38

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495 Table3. Concentration level of VOCs and compositions of major groups in Zhengzhou and other cities in China

	Guangzhou	Nanjing	Beijing	Hangzhou	Wuhan	Zhengzhou
Items	March-December, 2005	2011-2012	16-18 August, 2006	July-August, 2013	2013-2014	May-September, 2017
Sampling site	residents-commercial -transportation mixed area	transportation- industry mixed area	residents-commercial mixed area	residents- transportation mixed area	urban	urban
Quantified compounds	59 NMHC	56 NMHC	47 NMHC	56 NMHC	99 VOCs	56 NMHC
Total samples	145	—	24	—	—	400
TNMHC (ppbv)	47.3	43.5	65.55±17.44	55.9	23.3±0.5	29.18±23.08
<i>alkane</i>	49.0	45.0	52.3	33.2		56±12
<i>alkene</i>	16	25.3	21.2	25.9		16±7.6
<i>aromatic</i>	23	22.3	18.1	24.3		14±8.4
<i>alkyne</i>	12	7.3	8.4	16.6		13±6.7
Reference	Li and Wang, 2012	An et al, 2014	Guo et al, 2012	Li et al, 2017	Lyu et al, 2016	this study

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Table4. Specific information on VOCs, O₃ and NO at the four sites in June, 2017

Composition or conc.	JK	MEM	YH	GS
aromatic(%)	9.06	11.57	4.72	15.75
alkene(%)	6.36	4.13	5.52	5.47
ΣVOCs (ppbv)	34.02	30.28	28.33	39.29
O ₃ (ppbv)	74.87	73.50	73.81	87.99
NO(ppbv)	7.10	7.72	2.34	4.47

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Table5. Top 10 VOCs ranked according to calculated ozone formation potential (OFP)

JK			MEM			YH			GS		
species	OFP(ppbv)	(%)	species	OFP(ppbv)	(%)	species	OFP(ppbv)	(%)	species	OFP(ppbv)	(%)
Ethylene	18.99	25.54	Ethylene	18.44	30.88	Ethylene	19.83	28.10	Ethylene	18.04	25.96
Isoprene	12.99	21.83	Isoprene	4.66	10.10	Isoprene	7.44	11.30	Isoprene	8.01	16.75
m/p-Xylene ^a	6.08	5.89	Toluene	3.73	6.67	Toluene	6.63	7.75	Toluene	7.43	7.67
Toluene	5.53	5.83	Propylene	3.60	6.16	m/p-Xylene ^a	3.93	4.38	Propylene	4.39	5.85
Propylene	4.03	5.36	Acetylene	2.82	5.00	Acetylene	3.15	4.38	m/p-Xylene ^a	4.31	4.57
Acetylene	2.97	4.44	m/p-Xylene ^a	2.55	4.20	Propylene	3.01	3.60	Acetylene	2.76	4.24
n-Butane	2.15	3.05	n-Butane	1.81	3.20	Trans-2-pentene	2.25	2.94	n-Butane	1.82	2.93
o-Xylene	1.83	2.00	Isopentane	1.76	3.16	n-Butane	1.84	2.80	Isopentane	1.71	2.68
Isopentane	1.66	1.95	Ethane	1.58	2.96	Isopentane	1.59	2.22	Propane	1.38	2.26
Propane	1.17	1.73	Propane	1.31	2.48	Propane	1.18	1.98	Isobutane	1.13	1.98

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^a *m*-Xylene and *p*-Xylene are co-eluted in the chromatographic separation.

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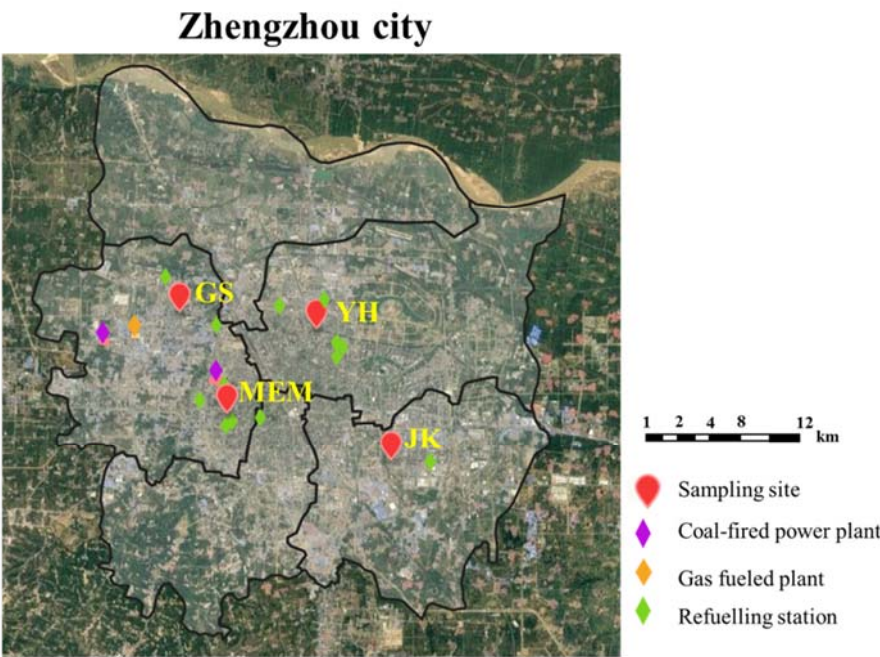


Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.

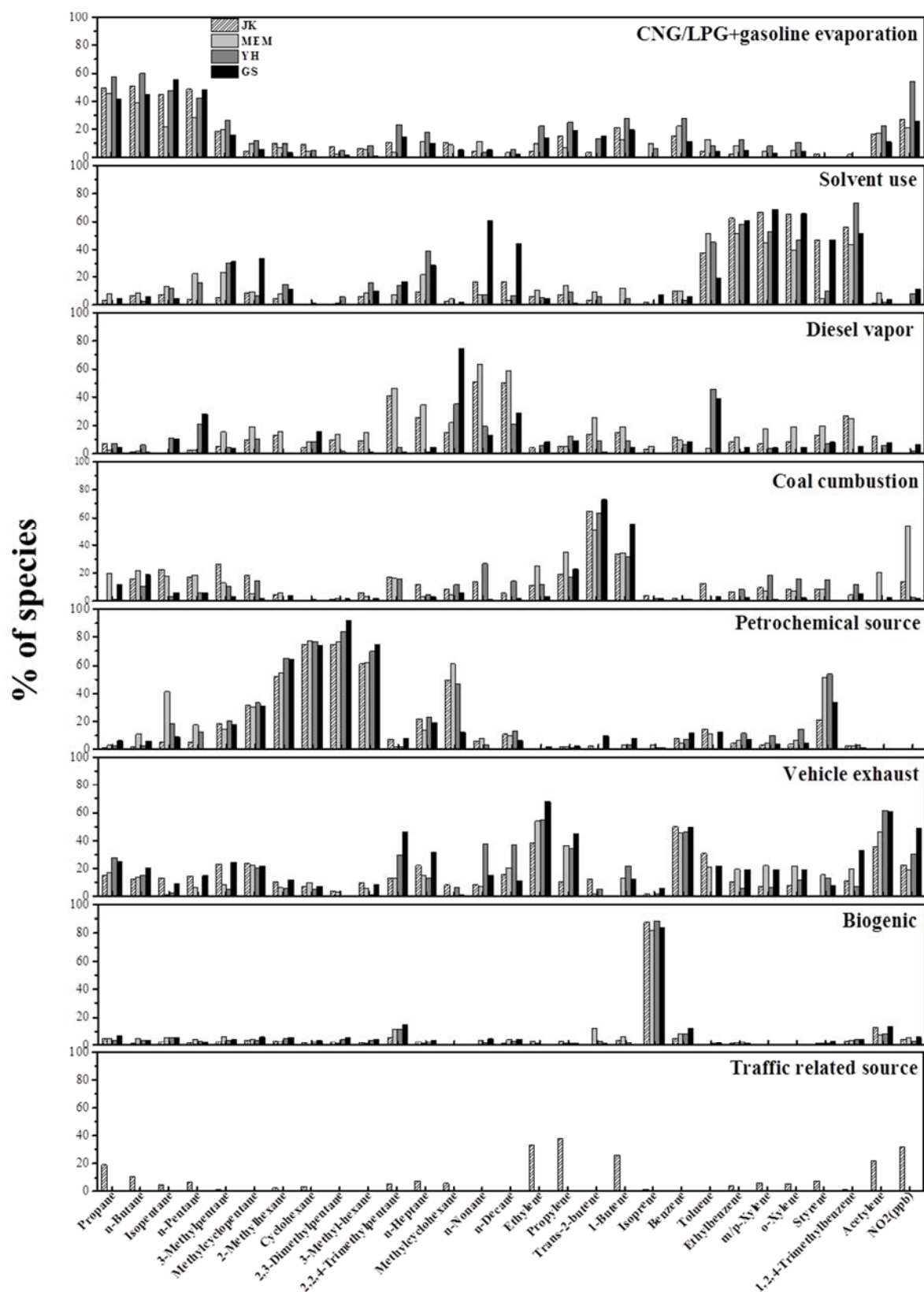


Fig. 2 Explained variations in source profiles as identified by PMF

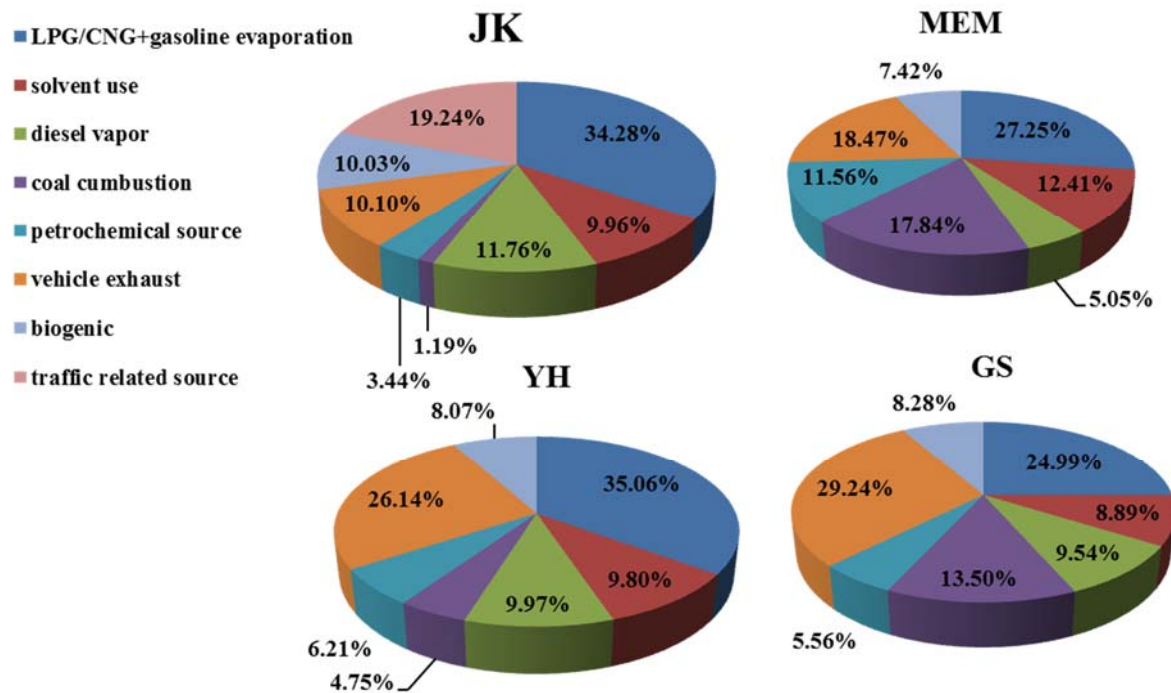


Fig. 3 Source apportionment results during the whole sampling period.

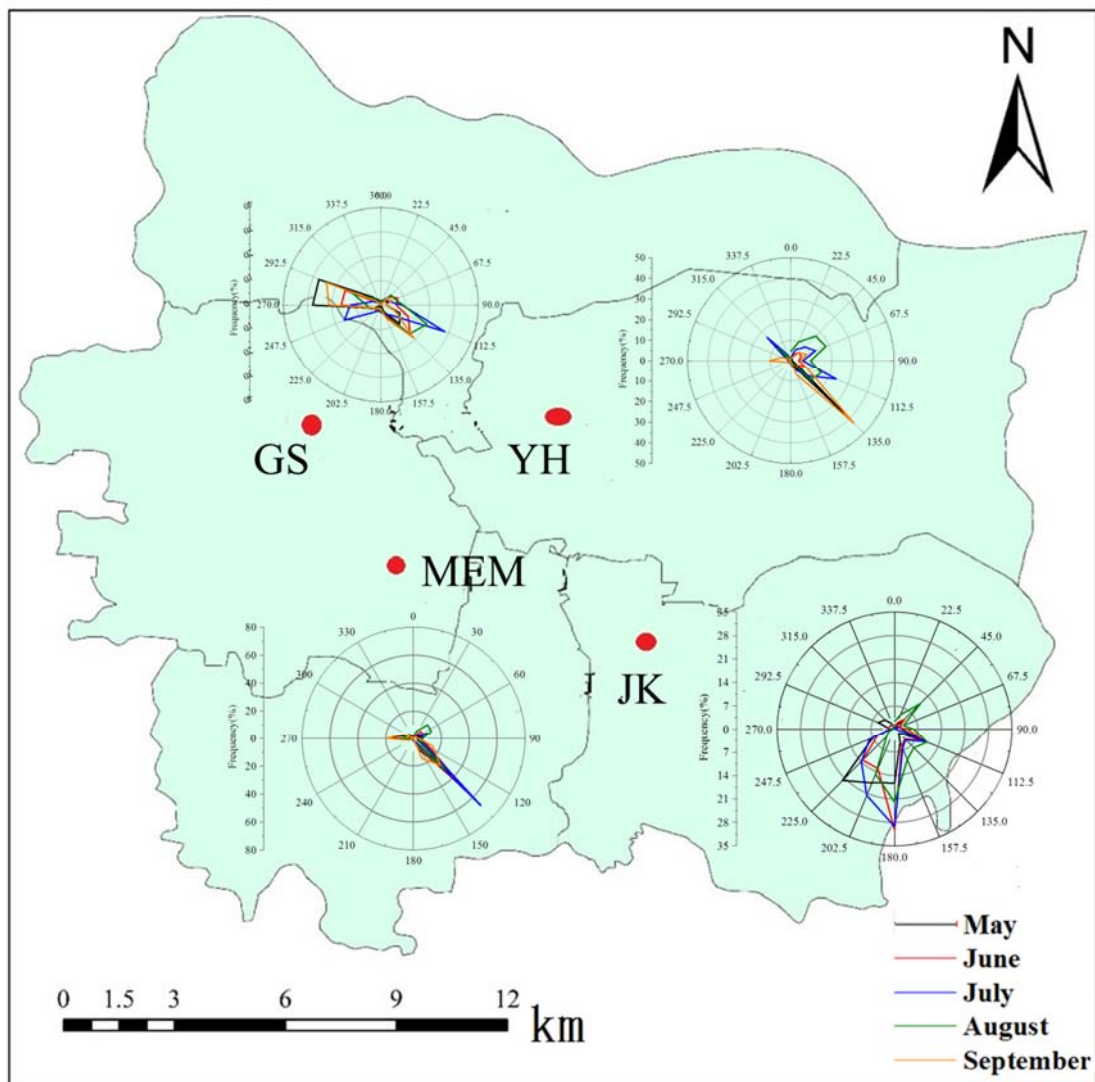
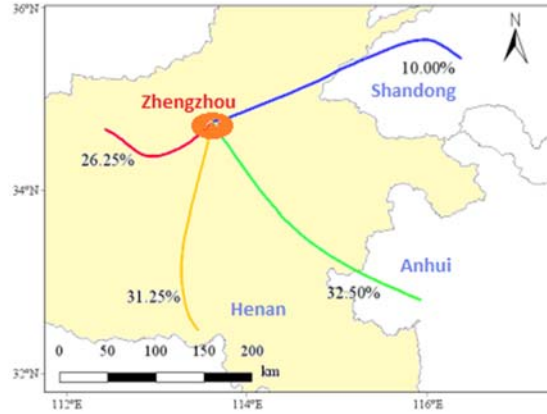
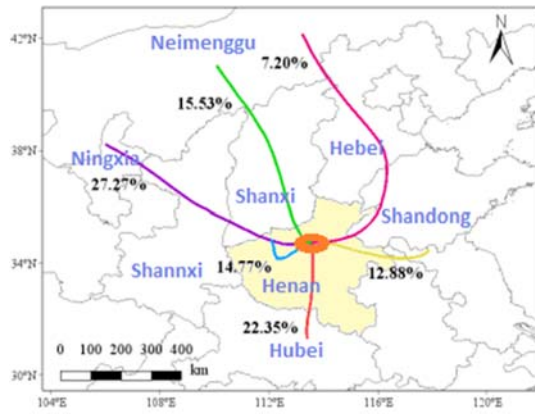


Fig.4 Wind direction for each site during May to September, 2017

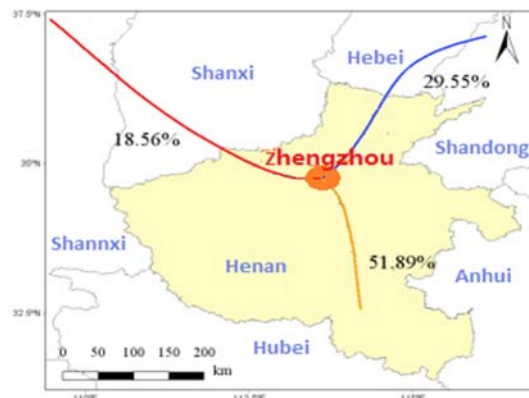
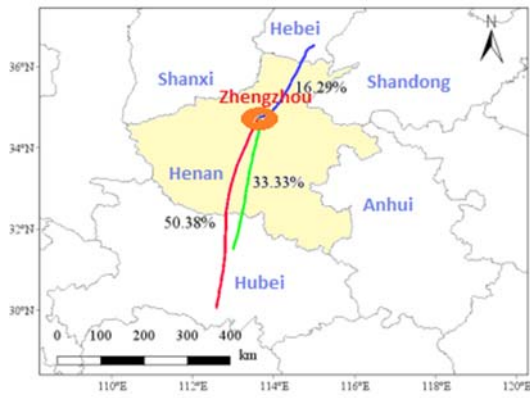
May

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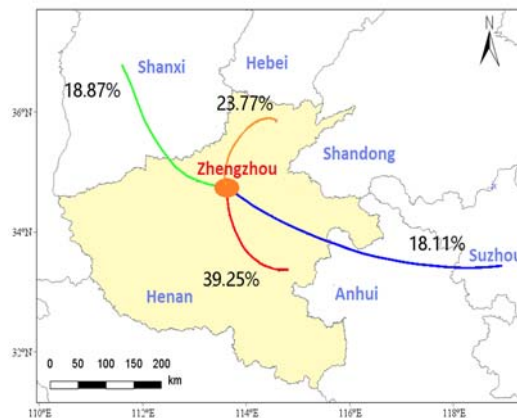


Fig. 5 Cluster analysis of Zhengzhou in each sampling month

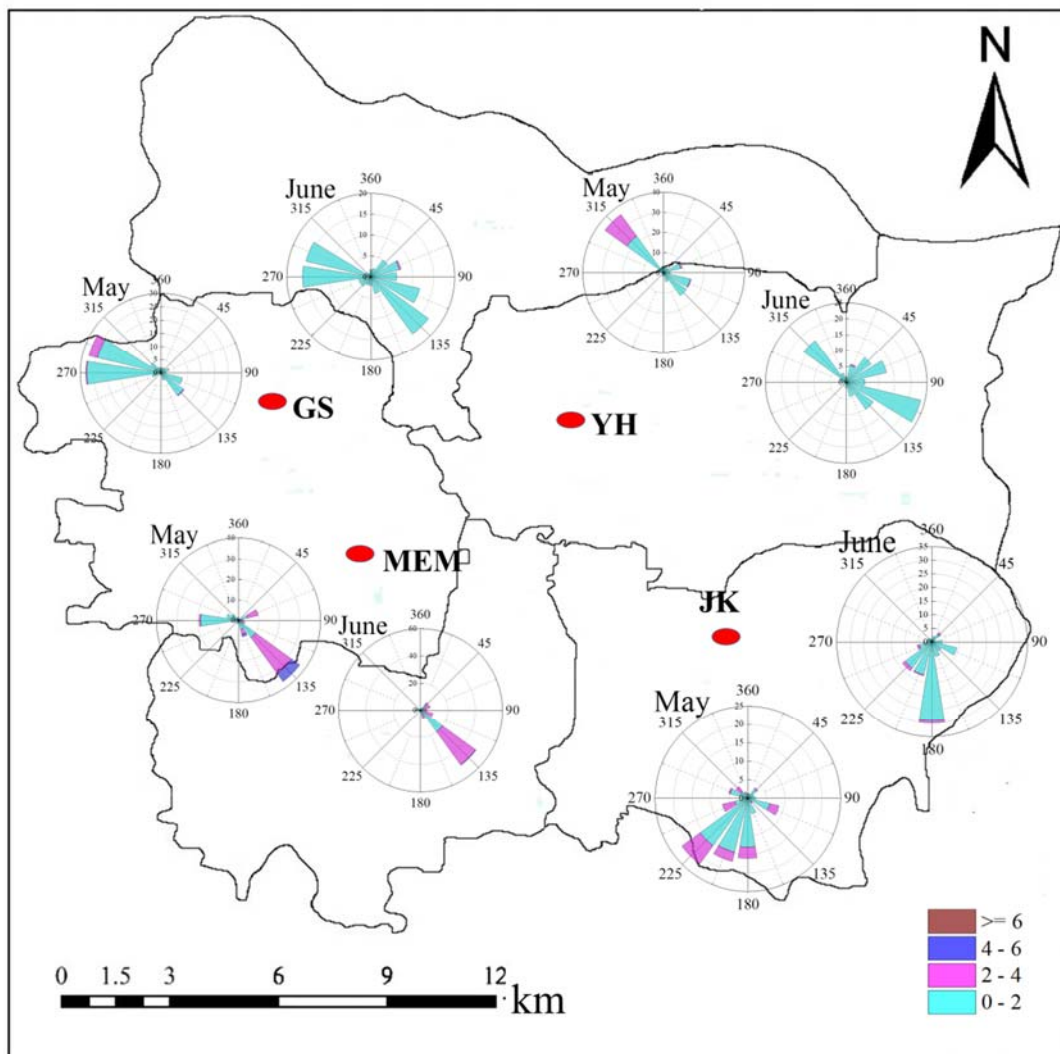


Fig. 6 Wind rose of each site in May and June (the wind distribution in other three months were illustrated in Fig S2)

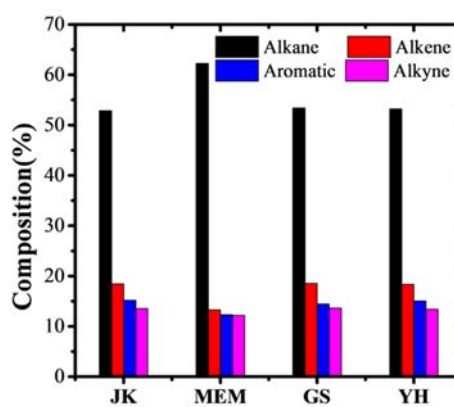
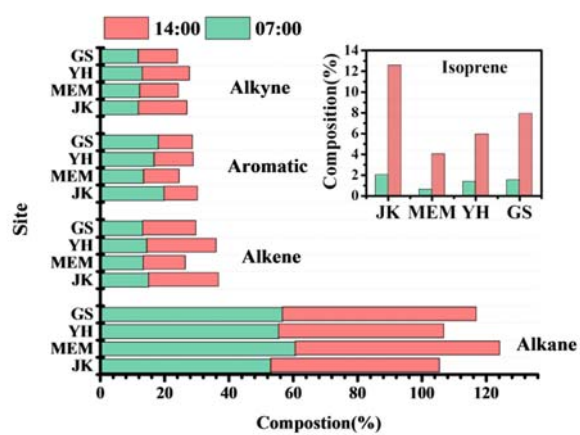


Fig. 7 Compositions of major organic classes at 07:00 LT, 14:00 LT (left) and that during the whole sampling period at the four sites

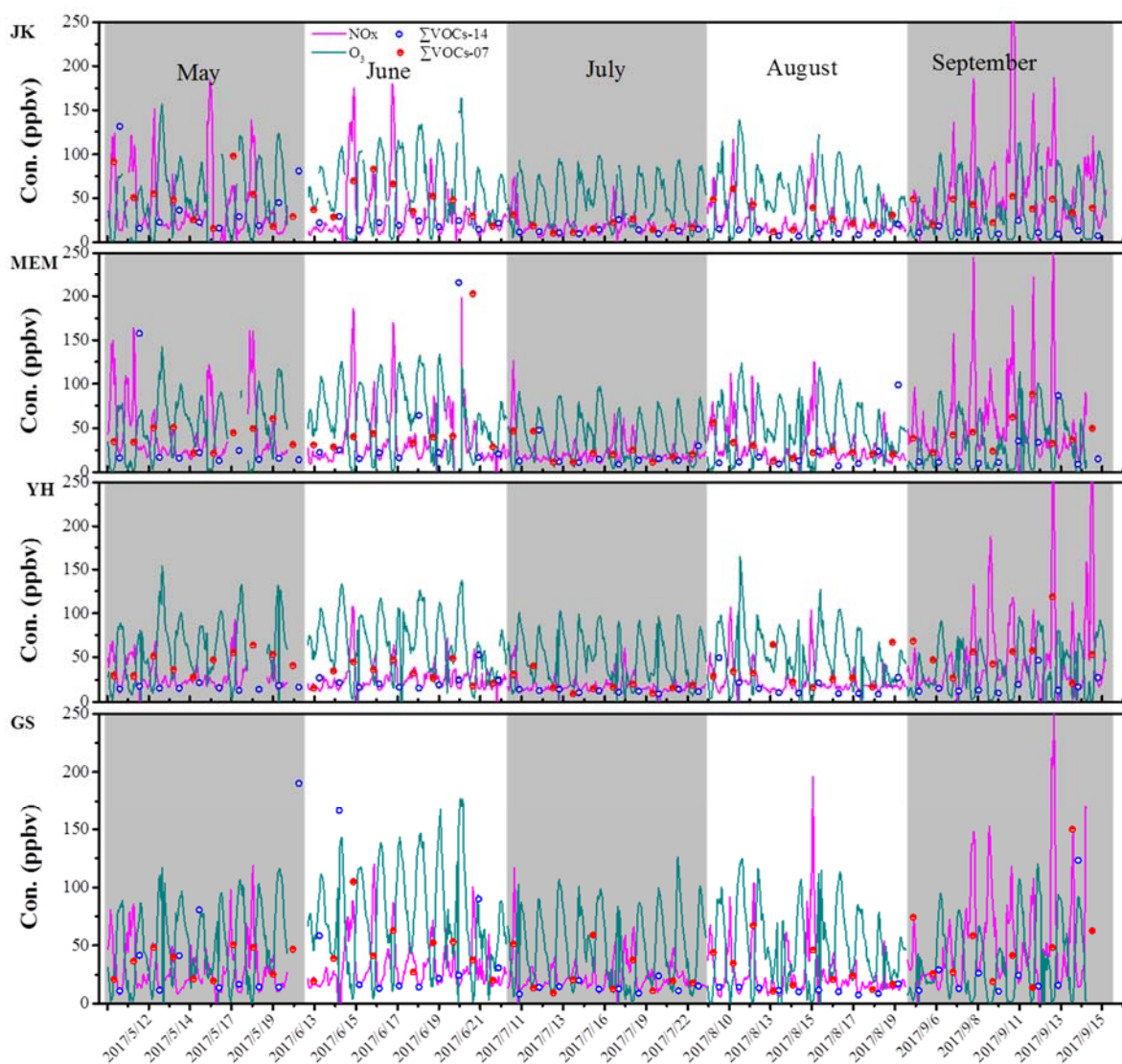


Fig. 8 Temporal variations of mixing ratios of ΣVOCs , NOx and O_3 at the four sites during the whole sampling period, in which $\Sigma \text{VOCs-07}$ stands for the concentration level of ΣVOCs observed at 07:00 LT, and $\Sigma \text{VOCs-14}$ was that observed at 14:00 LT.

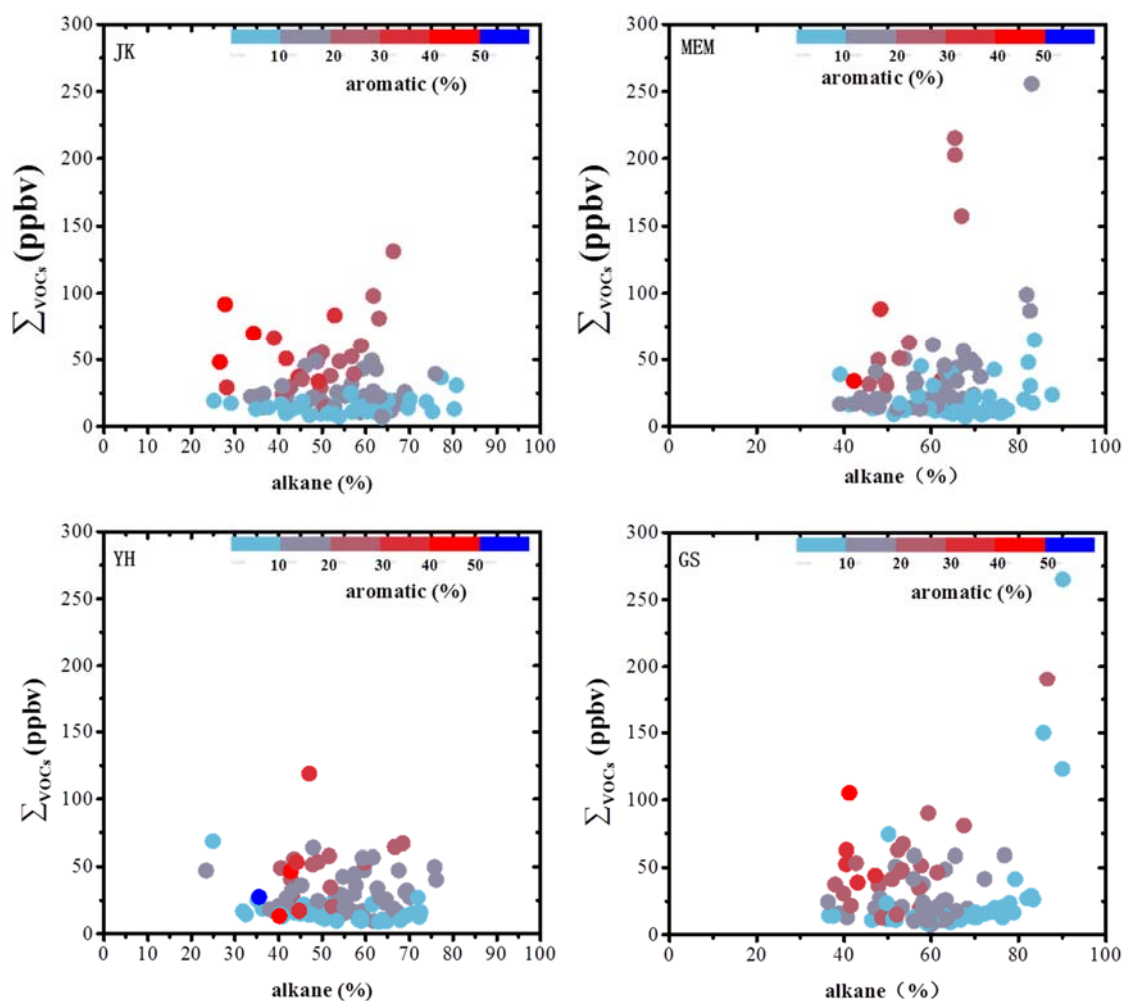


Fig. 9 The relationship between mixing ratio of ΣVOCs and the composition of alkane, the data points were color coded with the composition of aromatic.

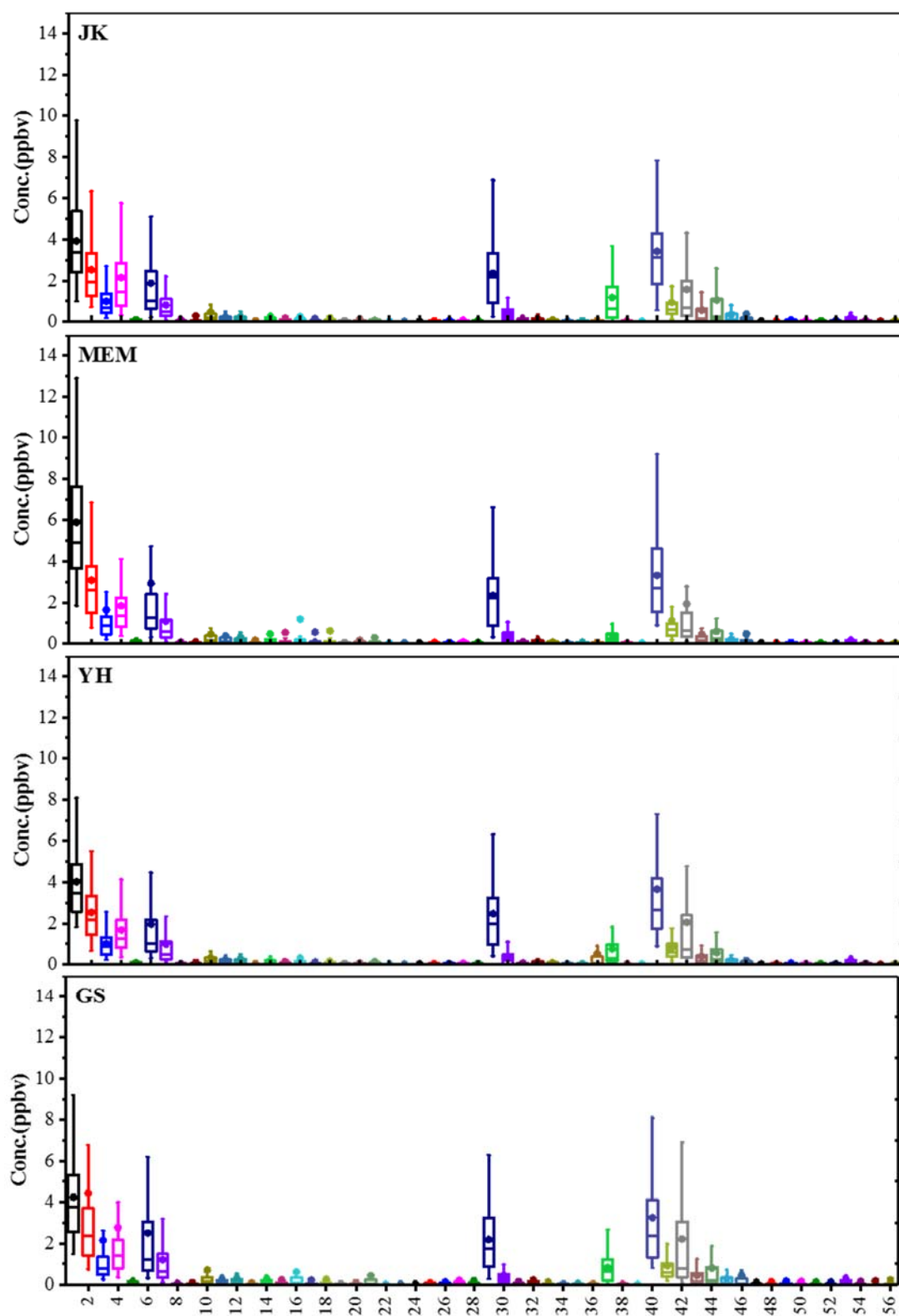
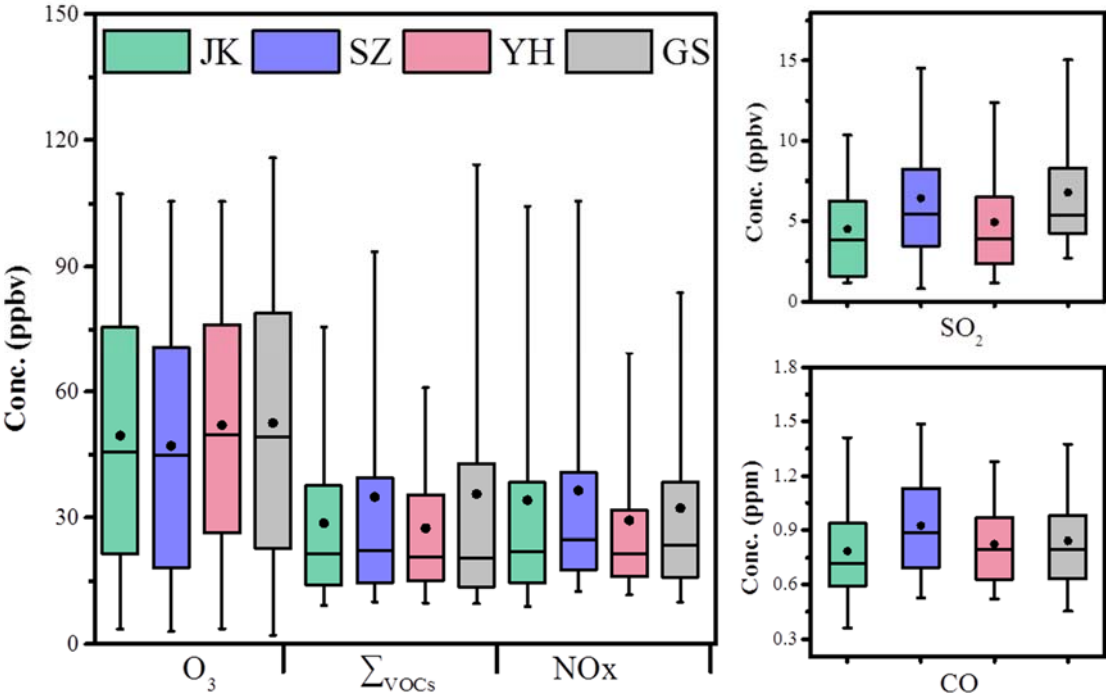


Fig.10 concentration level of 57 VOCs at each site for the whole sampling period, the whisker was ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in the box represent median value. The number of chemicals can refer from Table S1.



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541 Fig. 11 The distribution of concentration point on O₃, ΣVOCs, NO_x, SO₂ and CO at each site, the range of
542 the box was 25%-75%, the black line in the box stands for median level, the black dot represent the
543 average level, the range of whisker was 5-95%.

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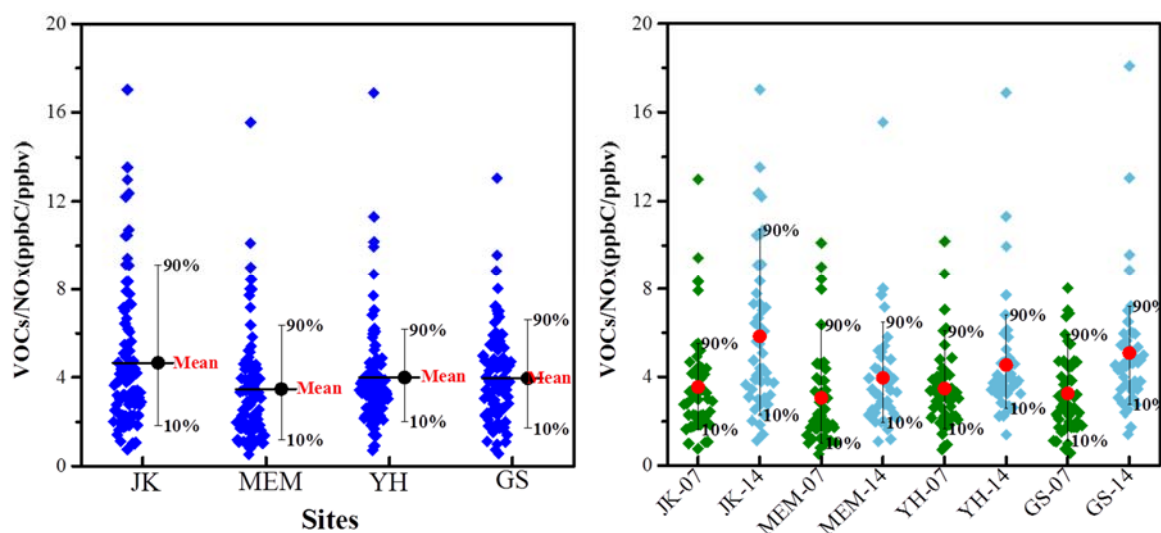


Fig.12 The data distribution of VOCs/NOx(ppbC/ppbv) at the four sites (left), and the ratio observed at 07:00 LT and 14:00 LT were presented as well (right).

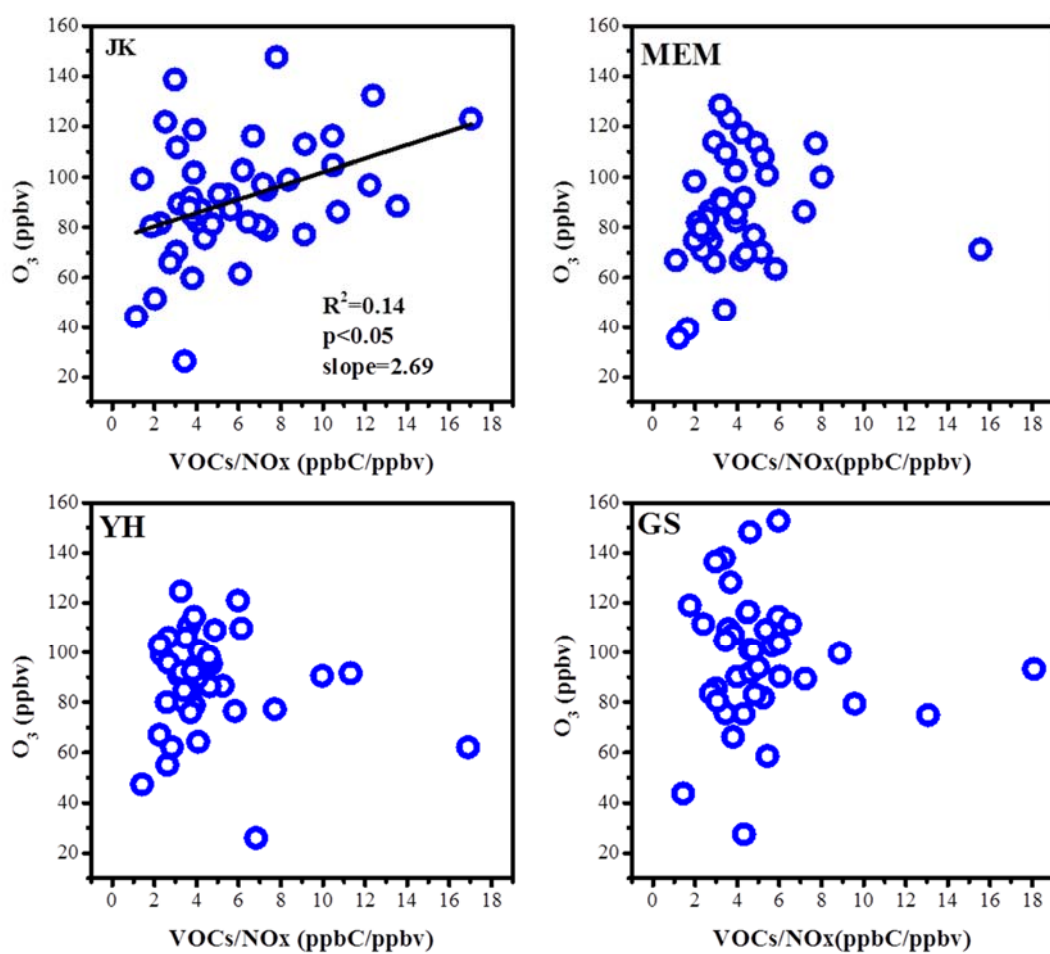


Fig.13 The relationship between O_3 and VOCs/NOx at 14:00 LT

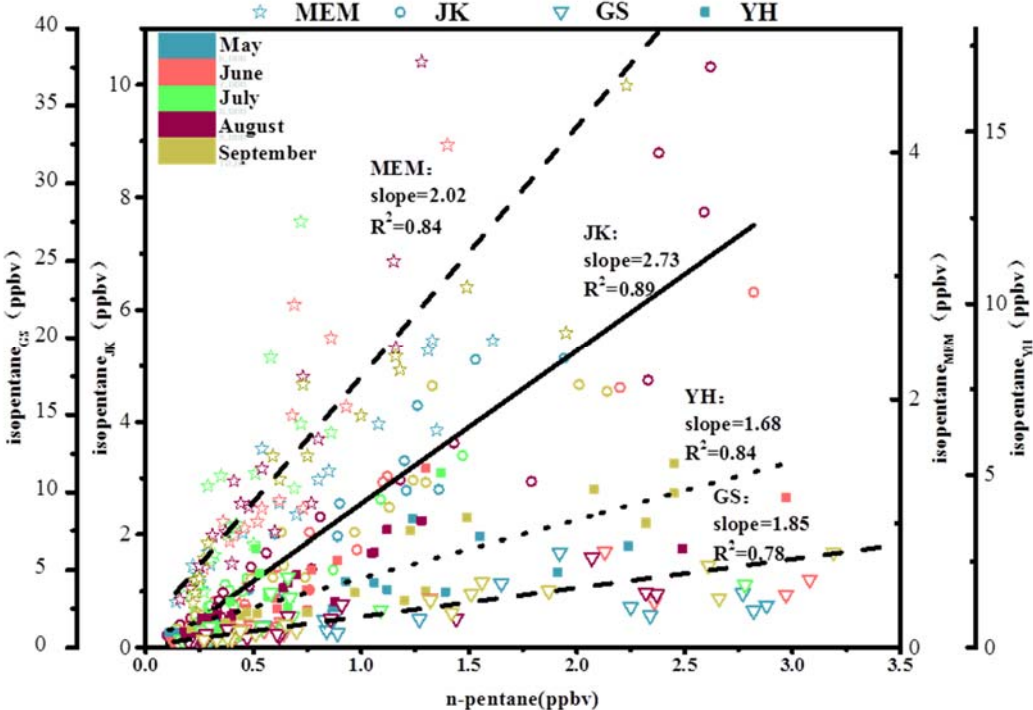


Fig. 14 Ratios of isopentane to n-pentane at every site

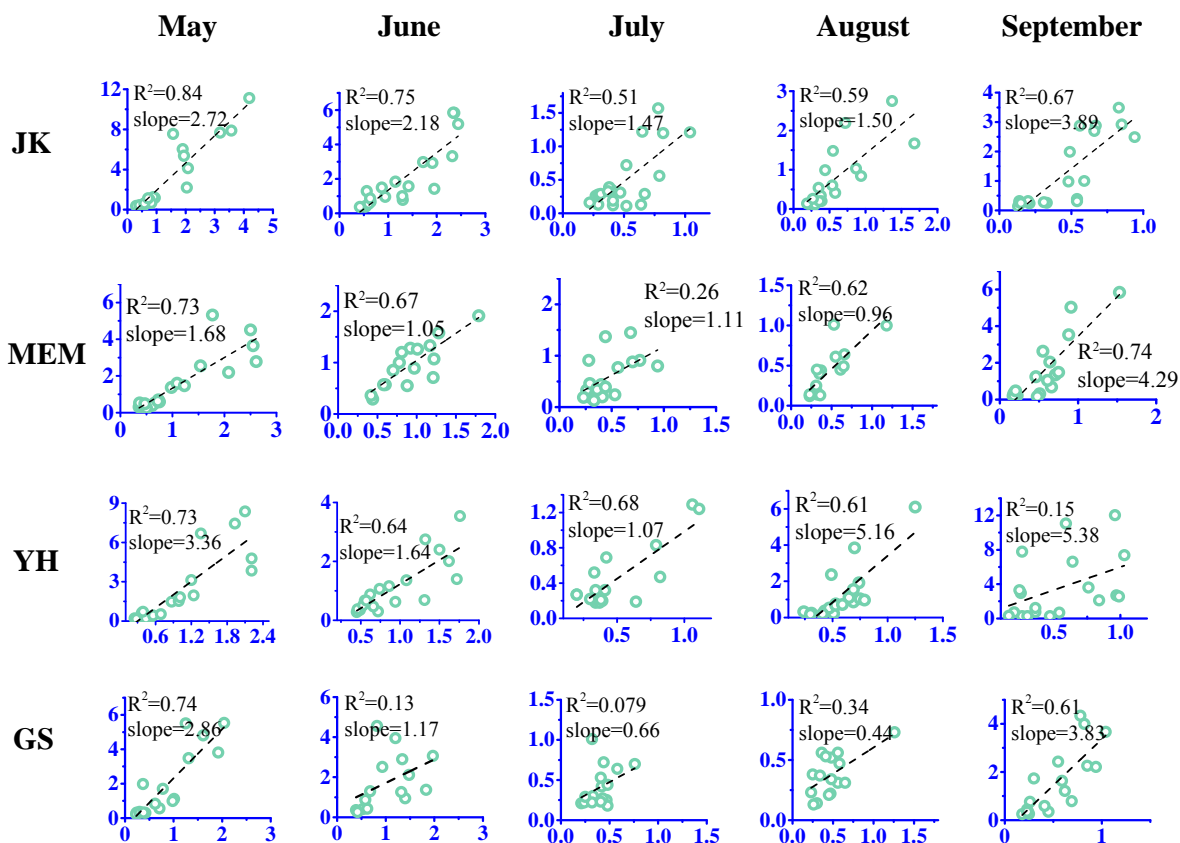


Fig.15 T/B ratios and the correlation analysis between benzene and toluene at every site from May to September, 2017. The vertical axis in every small figure represents the mixing ratio of toluene (ppbv), while the horizontal axis stands for benzene level (ppbv)

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