

1 Professor MacKenzie  
2 Editorial Office  
3 Atmospheric Chemistry and Physics

26<sup>th</sup> October 2018

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6  
7  
8 Dear Professor MacKenzie,

9  
10 Attached please find our revised manuscript entitled "Characterization of VOCs and their  
11 related atmospheric processes in a central China city during severe ozone pollution periods"  
12 (Manuscript number: acp-2018-397), as well as a thorough, point-by-point response to each point  
13 raised from the reviewers ("Response to Reviewers"). The revisions to the manuscript are  
14 highlighted in blue words in the provided Microsoft Word document. Additionally, there is a clean  
15 revised manuscript as required.

16  
17 We greatly appreciate those comments and valuable suggestions from the reviewers. The  
18 manuscript has been greatly improved. We do feel that we have demonstrated our efforts in the  
19 revised manuscript.

20  
21 Please do not hesitate to contact me at [stevenho@hkpsrl.org](mailto:stevenho@hkpsrl.org) or by phone at  
22 +00-852-66833994 if you need additional information. Thank you for your time in handling our  
23 manuscript.

24  
25 Sincerely,

26  
27 Steven S.H. Ho, Ph.D.  
28 Principal Scientist  
29 Division of Atmospheric Sciences  
30 Desert Research Institute  
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34

35

36 **Comment and response #1**

37 The authors thank for all valuable comments and suggestions to our manuscript.  
38 We have point-to-point response to each comment as below.

39 **Comment 1:**

40 The title can also be changed, since the influence of VOCs on O<sub>3</sub> formation forms  
41 only a small part of the paper. The main focus of the paper is on the measured VOCs.

42 **Response:**

43 Thanks for the suggestion, the title has been revised as:

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

46 **Comment 2:**

47 I am not sure about the use of this acronym for the 57 VOCs. A VOC is a species and  
48 PAMS is not

49 **Response:**

50 The term has been replaced by “VOCs”.

51 **Comment 3:**

52 A high VOC/NO<sub>x</sub> ratio usually signifies that an area is NO<sub>x</sub> sensitive and not VOC  
53 sensitive. Changes in VOC concentration do therefore not cause any changes in O<sub>3</sub>  
54 concentrations, while increased NO<sub>x</sub> causes increased O<sub>3</sub>.

55 **Response:**

56 According to the ratio of VOCs /NO<sub>x</sub>, the ozone formation regime was prone to  
57 VOC-limited. The statement has been revised accordingly.

58 **Comment 4:**

59 Which four sites? Where you measured VOC precursor species? You mentioned that  
60 VOCs were measured in Zhengzhou City and precursor species were measured at four  
61 different sites

62 **Response:**

63 This refers to the four sites located in Zhengzhou city where we collected the samples  
64 in this study. The details of sampling location have been described in the main texts.

65 **Comment 5:**

66 A VOC-limited regime is associated with low VOCs not high VOCs. Your high  
67 VOC/NO<sub>x</sub> ratio indicate a NO<sub>x</sub> limited regime and therefore NO<sub>x</sub> must be reduced  
68 and not VOCs to reduce O<sub>3</sub>. However, I think this area is VOC-limited (very high  
69 NO<sub>x</sub>) and reduction on VOCs will result in reduced O<sub>3</sub>. And therefore your high  
70 VOC/NO<sub>x</sub> ratio does not make sense

71 **Response:**

72

73 Sorry for the unclear description in previous statement. Yes, it should be VOC-limited.  
74 The related statements have been revised.

75 **Comment 6:**

76 Fuel evaporation? Solvent evaporation, I agree with.

77 **Response:**

78

79 Solvent (i.e., from industry and household) is a major source of VOCs definitely,  
80 while fuel evaporation is also a contributor to VOCs originated from industries or  
81 other sources powered by fossil fuels.

82 **Comment 7:**

83 Where? In the USA or in China?

84 **Response:**

85 This refers to worldwide countries, including China and USA.

86 **Comment 8:**

87 This sentence read that the nationwide deterioration of air quality contributes the  
88 measurements being scarce. Please improve.

89 **Response:**

90 We have revised the sentence as

91 *“In China, the investigations on VOCs including source apportionment,*  
92 *measurement of emission profiles and interpretation of seasonal variations were*  
93 *mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and*  
94 *Beijing-Tianjin (BJT) regions (An et al., 2014; Wang et al., 2014; Chen et al.,*  
95 *2014; Liu et al., 2016a; Guo et al., 2017). Limited studies have been conducted in*  
96 *less developed or developing regions (i.e., southwestern and northwestern China)*  
97 *where prominently impacted by biomass burning and with high abundances of*  
98 *toxic and reactive compounds. (Li et al., 2014; Li et al., 2017a).”*

99 **Comment 9:**

100 These sites are only in the USA

101 **Response:**

102 The term of PAMS was widely used to present the most critical contributors in the  
103 production of ozone in the atmosphere. It does not mean the sampling sites.

104 **Comment 10:**

105 This sentence does not fit within the context of this paragraph that is focusing on  
106 VOC measurement in China and the gaps in knowledge.

107 **Response:**

108 The original lines 64-66 have been deleted

109 **Comment 11:**

110 why? Due to VOCs/CO or NO<sub>x</sub>?

111 **Response:**

112 The statement has been revised as

113 *"In less developed cities of Heilongjiang and Anhui, biomass combustion had the*  
114 *highest contribution (40% and 36%, respectively) to the O<sub>3</sub> formation potentials*  
115 *due to high quantity of agricultural activities."*

116 **Comment 12:**

117 The first two paragraphs are not well structure and must be improved.

118 **Response:**

119 The paragraphs have been revised, specified in newly lines 37-74.

120 **Comment 13:**

121 Why? Due to increased NO<sub>x</sub> emissions?

122 **Response:**

123 The sentence has been revised as:

124 *"The percentage of VOC-limited regime in North China Plain (NCP) increased*  
125 *from 4% to 6% between 2005-2013, owing to the rapid increases of NO<sub>x</sub>*  
126 *emissions (Jin and Holloway, 2015)."*

127 **Comment 14:**

128 please improve

129 **Response:**

130 The sentence has been revised as:

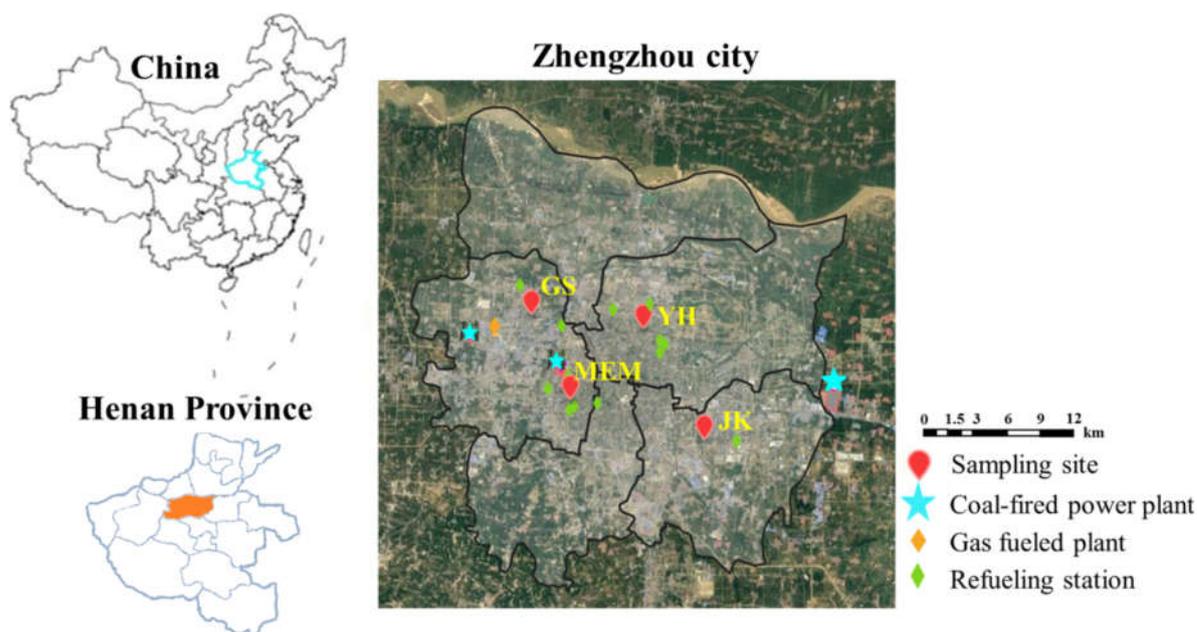
131 *“Based on the density of population distribution, locations of industrial facilities,*  
132 *and the prevailing winds, four sites have been selected for sample collection.”*

133 **Comment 15:**

134 If possible, it would be nice to show the major pollutant sources on the map in Fig. 1.  
135 This will help a lot with interpretation of results e.g. discussion in Section 1 on the  
136 influence of wind direction on the different  $\Sigma$ VOCs measured at each of the sites for  
137 all the months.

138 **Response:**

139 This is a good idea. Suggestion taken. The map was improved as below:



140

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

142 **Comment 16:**

143 Please better explain. Why only 10 days? Were there only ten days in each month that  
144 it did not rain?

145 **Response:**

146 The sentence has been revised as:

147 *“Ten sampling days with the rainfall record (ca. 0 mm) were chosen in every*  
148 *month during the period of May - September, 2017 consequently, to represent a*  
149 *typical air quality condition in a month.”*

150 **Comment 17:**

151 What was considered to be valid samples?

152 **Response:**

153 “Valid samples” means that those samples were not influenced by high humidity,  
154 wrong operation, and fault of instrument.

155 **Comment 18:**

156 I do not think that this is a good acronym for your VOC species studied

157 **Response:**

158 Suggestion taken. The term has been replaced in the whole manuscript.

159 **Comment 19:**

160 According to what? Why were only these species considered relevant? Also, I assume  
161 from the rest of the discussion in the paper, these 57 species are only hydrocarbons.  
162 Therefore rather say that the 57 species included 28 were alkanes, 11 alkenes,  
163 acetylene and 17 aromatics.

164 **Response:**

165 The sentence has been revised as:

166 *“The standard gas of PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to*  
167 *construct the calibration curves for the 57 target VOCs, including 28 alkanes, 11*  
168 *alkenes, acetylene and 17 aromatics”*

169 **Comment 20:**

170 This sentence and table is not necessary in the document and can be removed.  
171 Although it could be included a supplementary material, I do not think these  
172 analytical specifications contribute to the main content of this paper.

173 **Response:**

174 Thanks for the suggestion. It has been moved to supporting information, depicted as  
175 Table S1.

176 **Comment 21:**

177 Uncertain what is meant here.

178 **Response:**

179 The statement has been revised as:

180 *“No obvious disturbances due to improperly activities (such as smoking, spray*  
181 *fumes, etc.) of sample collectors were present during the sampling events.”*

182 **Comment 22:**

183 Not sure that this is the correct term

184 **Response:**

185 The term has been replaced by “QC/QA” and moved to supporting information.

186 **Comment 23:**

187 Unnecessary

188 **Response:**

189

190 It has been deleted

191

192 **Comment 24:**

193 Please improve the description of the PMF technique (line 166 - 184) Look at the  
194 paper Jaars, et al., Atmospheric Environment, 172 133–148, 2018,  
195 <http://dx.doi.org/10.1016/j.atmosenv.2017.10.047>.

196 **Response:**

197 Thanks for the reference. The description has been revised.

198

199 **Comment 25:**

200 Please structure this entire Section better. Numerous examples of incoherent writing is  
201 illustrated in the paragraphs in this section.)

202 **Response:**

203 The section has been revised.

204 **Comment 26:**

205 Air mass does not originate but pass over a source region/city/sources.

206 **Response:**

207 The statement has been revised as:

208 *“In May, the largest cluster (27.2%) was passed over from Yinchuan, a central*  
209 *city in northwest China.”*

210 **Comment 27:**

211 It will be better here to say that the  $\Sigma_{VOCs}$  different for all the months at all the sites,  
212 with the site with highest  $\Sigma_{VOCs}$  not being the same each months. This can be  
213 attributed to numerous factors that will be explored later in the paper. And then you  
214 can present the influence of prevalent wind direction on concentrations measured.

215 **Response:**

216 The related section has been revised according to the suggestion, specified as:

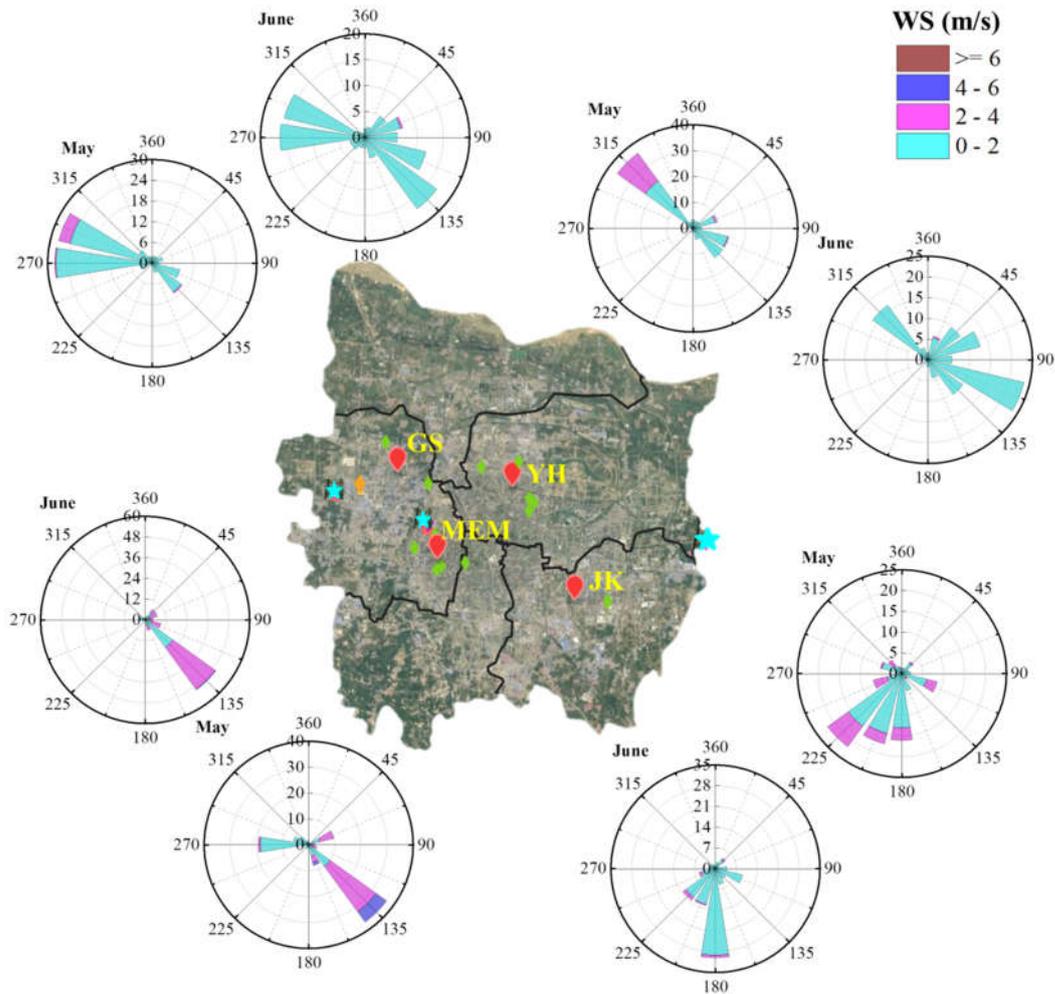
217 *“The  $\Sigma_{VOCs}$  varied at the four sites, where the highest  $\Sigma_{VOCs}$  and their*  
218 *compositions were not identical across the sampling months as well. In May 2017,*  
219 *the highest  $\Sigma_{VOCs}$  was reported at JK ( $37.65\pm 22.58$  ppbv), followed by GS*  
220 *( $31.73\pm 18.70$  ppbv), YH ( $30.05\pm 16.43$  ppbv) and MEM ( $29.05\pm 15.34$  ppbv),*  
221 *while the  $\Sigma_{VOCs}$  values for the month of June, July, August and September were*  
222 *found to be in the order of: GS>JK>MEM>YH, MEM>GS>JK>YH,*  
223 *YH>MEM>JK>GS, and MEM> YH > GS >JK, respectively. This can be*  
224 *attributed to numerous factors that will be explored later in the paper. Besides*  
225 *the emission sources (to be discussed in Section 3.2), the impacts controlled by*  
226 *meteorological conditions should not be ignored as well.”*

227 **Comment 28:**

228 This discussion on the influence of prevailing wind direction and -speed could be  
229 significantly improved with an appropriate wind rose overlaid on a map of the city  
230 indicating the four sites and the major sources.

231 **Response:**

232 They have been presented in Fig. 4 and Fig S2.



233

234 Fig.4 Wind rose at each site in May and June (the wind distribution in other three months were  
 235 illustrated in Fig S2)

236

237 **Comment 29:**

238 Can you indicate this on a topographical map of the city?

239 **Response:**

240 A reference contained the topographical map has been added.

241 *“Mu, B., Mayer, A. L., He, R., and Tian, G.: Land use dynamics and policy*  
 242 *implications in Central China: A case study of Zhengzhou, Cities, 58, 39-49,*  
 243 *10.1016/j.cities.2016.05.012, 2016.”*

244 **Comment 30:**

245 from where

246 **Response:**

247 The statement has been removed because of the adjustment of the newly Table 1 and  
248 Fig. 8.

249 **Comment 31:**

250 A figure with meteorological data for the sampling period must be included to assist  
251 in the discussion of the data.

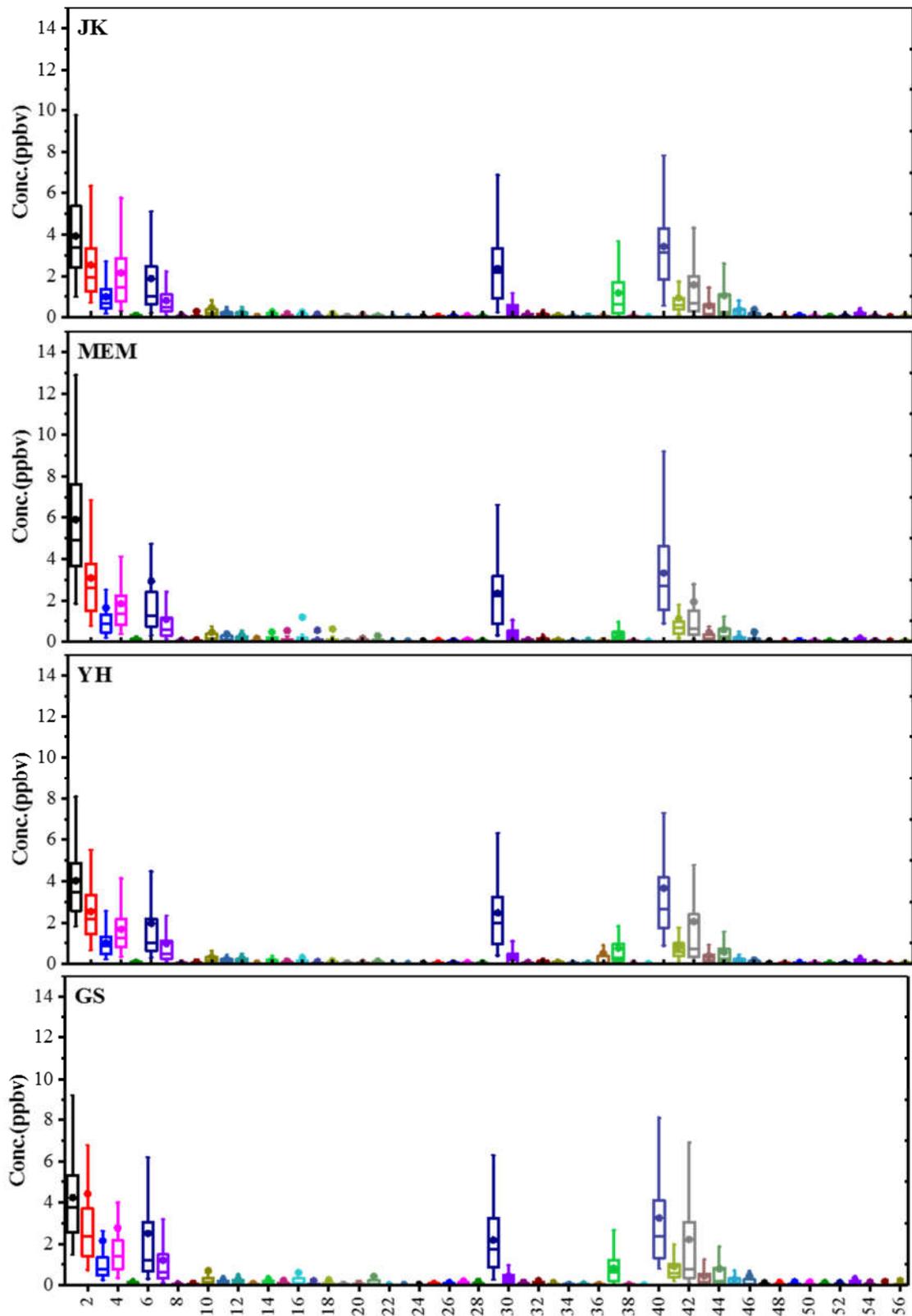
252 **Response:**

253 The statement has been removed because of the adjustment of the newly Table 1 and  
254 Fig. 8, and the meteorological data was presented in Fig S1.

255 **Comment 32:**

256 The authors must consider to rather include a figure with the statistical distributions  
257 (e.g. box and whisker plots with mean, median, as well as 25th, 75th percentiles) of  
258 the VOC species presented for the entire sampling period instead of the large Table 3.  
259 This will greatly assist in the discussion of concentrations measured at different sites.  
260 Table 3 could then only include the  $\Sigma$ VOC for each month at each of the site if they  
261 want to elaborate on the influence of wind direction and -speed on VOC  
262 concentrations measured at each site.

263 **Response:** Thanks for the suggestion, Fig.8 has been added.



264

265 Fig.8 Concentrations of 57 VOCs at each site for the whole sampling period, the whisker was  
 266 ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in  
 267 the box represent median value. The number of chemicals can refer from Table S1.

268 **Comment 33:**

269 Nowhere in the text it is indicated that these 57 VOCs were classified into alkane,  
270 alkenes, alkynes and aromatics, which are further discussed

271 **Response:**

272 The statement has been revised as

273 *“The standard gas of PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to*  
274 *construct the calibration curves for the 57 target VOCs, including 28 alkanes, 11*  
275 *alkenes, acetylene and 17 aromatics.”*

276 **Comment 34**

277 why is this?

278 **Response:**

279 It was attributed to the busy traffic in urban city. The sentence was revised as

280

281 *“With regard to the weight percentage of major groups (Table 3), the composition*  
282 *of alkanes was the largest in all cities because of their longer lifetimes and*  
283 *widespread from a variety of pollution sources (Fig. 5)”*

284 **Comment 35:**

285 Which will be nicely indicated in figure as suggested above presenting the statistical  
286 data of all VOCs measured at all the sites.

287 **Response:**

288

289 Suggestion taken. It has been presented in Fig.S3.

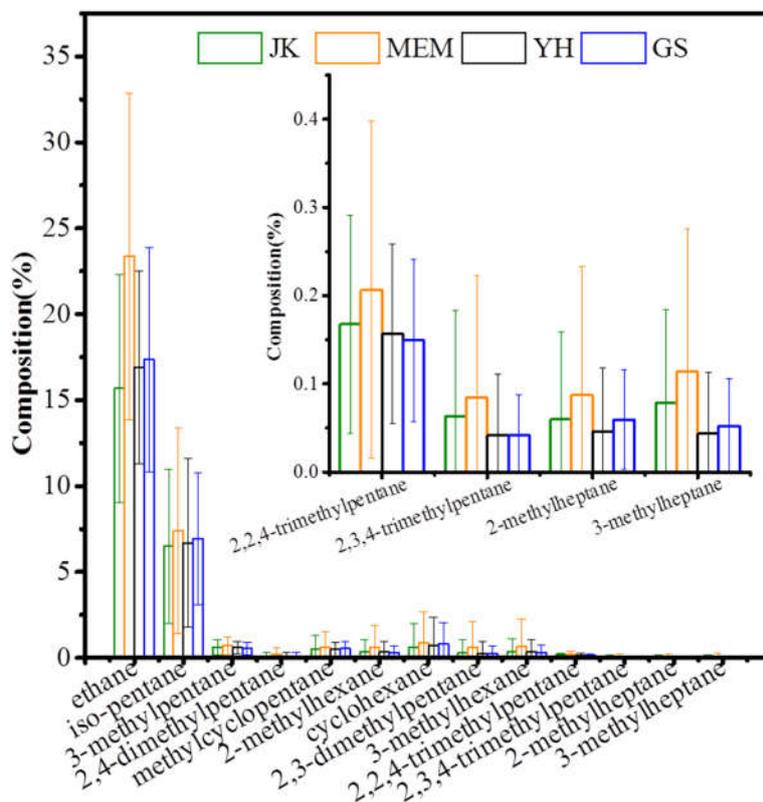


Fig. S3 Compositions of ethane, iso-pentane and C<sub>7</sub>-C<sub>8</sub> alkanes at JK, MEM, YH and GS

**Comment 36:**

What compounds? Alkanes in general, or the species contributing to alkane levels at MEM only? If the latter, why not elaborate on alkanes at the other sites?

**Response:**

They referred to ethane, isopentane and alkanes with 7-8 carbon atoms, which have been presented in Fig.S3.

**Comment 37**

missing an introductory sentence on the daytime and night-time concentration that is additionally presented in figure2

**Response:**

It was revised as:

*“Due to the variations of the planet boundary layer (PBL) height, solar radiation and emission sources, 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 at 14:00 LT (Fig. 5), because of the increased planet boundary layer*

310 *and the active photochemical reactions, while alkenes always peaked in the 14:00*  
311 *LT.”*

312 **Comment 38**

313 how so?

314 **Response:**

315 The statement has been revised as

316 *“According to the dataset, the increases in alkene compositions (~4.3% uplift)*  
317 *were mainly due to higher contributions of isoprene (~1.4% at morning and 7.6%*  
318 *in the afternoon), which was mainly emitted from biogenic sources and increased*  
319 *exponentially with ambient temperature (Jiang et al., 2018).”*

320 **Comment 39:** Please include a table where in these VOC results can be  
321 contextualized and compared to other cities. Only Beijing, Nanjing and Guangzhou  
322 included in Figure 2. Furthermore, the fact that concentrations for these three cities  
323 are included in Fig.2 are also not properly introduced in the text.

324 **Response:**

325 The information has been added in revised Table 3.

326 **Comment 40:**

327 Are you speaking generally here, i.e. all the cities in China?

328 **Response:**

329 It refers to the countries discussed here.

330 **Comment 41**

331 Here again you mention aromatics. An examples of a sentence "coming from  
332 nowhere" within the context of a paragraph that is trying to contextualize results.

333 **Response:**

334 The statement has been revised as

335 *“With regard to the weight percentage of major groups (Table 3), the*  
336 *composition of alkanes was the largest in all cities because of their longer*  
337 *lifetimes and widespread from a variety of pollution sources (Fig. 5), while the*  
338 *composition of aromatics was lower than alkenes in these cities except for*  
339 *Guangzhou.”*

340 **Comment 42:**

341 You are only comparing your results to the three cities included in Fig. 2 and not all  
342 the cities listed here in your discussion above

343 **Response:**

344 The results have been shown in Table 3.

345 **Comment 43:**

346 Reference of biofuel as source of acetylene

347 **Response:**

348 A reference has been added.

349 *“Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L.,*  
350 *Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile*  
351 *organic compounds and the influence of biomass burning at a rural site in*  
352 *Northern China during summer 2013, Atmospheric Environment, 124, 156-165,*  
353 *10.1016/j.atmosenv.2015.08.097, 2016.”*

354 **Comment 44:**

355 The problem with the dataset is that it does not cover a full year, i.e. all seasons.  
356 Therefore rather combine local (wind direction and -speed as done in Section 3.1) and  
357 long-range transport (back trajectories as done in Section 3.7) here to explain  
358 temporal variation.

359 **Response:**

360 Suggestion taken.

361 **Comment 45:**

362 better to have meteorological parameters in separate fig as indicated in previous  
363 comment.

364 **Response:**

365 It has been presented in Fig S1

366 **Comment 46:**

367 Are you sure it is for all pollutants?

368 **Response:**

369 It refers to air pollutants we monitored in this study, including SO<sub>2</sub>, CO, NO<sub>2</sub>, O<sub>3</sub> and  
370 VOCs. We have revised the statement as

371 *“The time series of mixing ratios of NO<sub>x</sub>, O<sub>3</sub> and ΣVOCs at every site are shown in*  
372 *Fig. 6. The results showed a distinctive temporal characteristic where lower*  
373 *levels of SO<sub>2</sub>, CO, NO<sub>x</sub>, O<sub>3</sub> and ΣVOCs were observed in July and August*  
374 *(mid-summer) (Table S5).”*

375 **Comment 47**

376 You did not collect VOCs on rainy days as indicated in your experimental section.

377 **Response:**

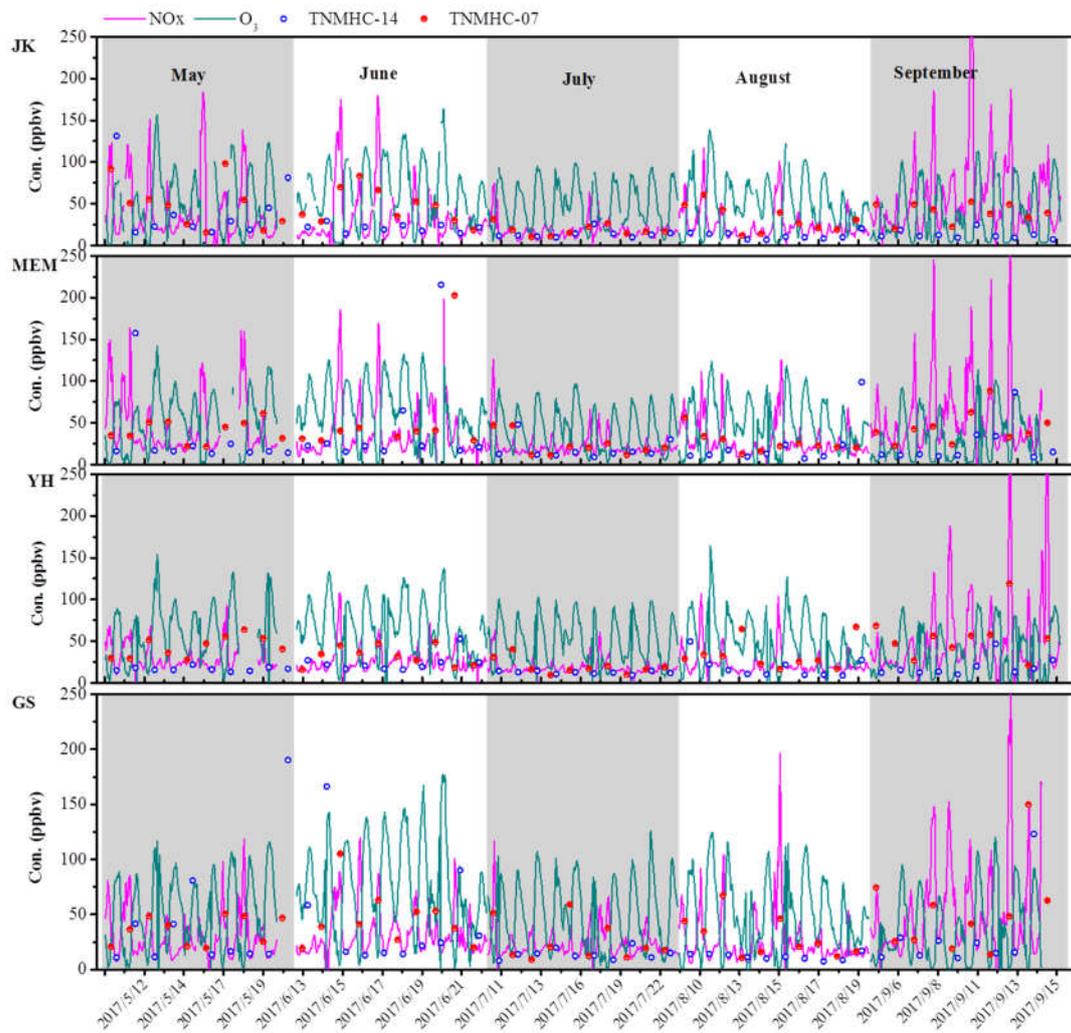
378 Yes, this observation was referred to the results from other studies.

379 **Comment 48:**

380 This is very difficult to see in Fig. 3. Fig. 3 must be improved to be more legible and  
381 easier to observe observations

382 **Response:**

383 It has been changed to newly Fig 6.



384

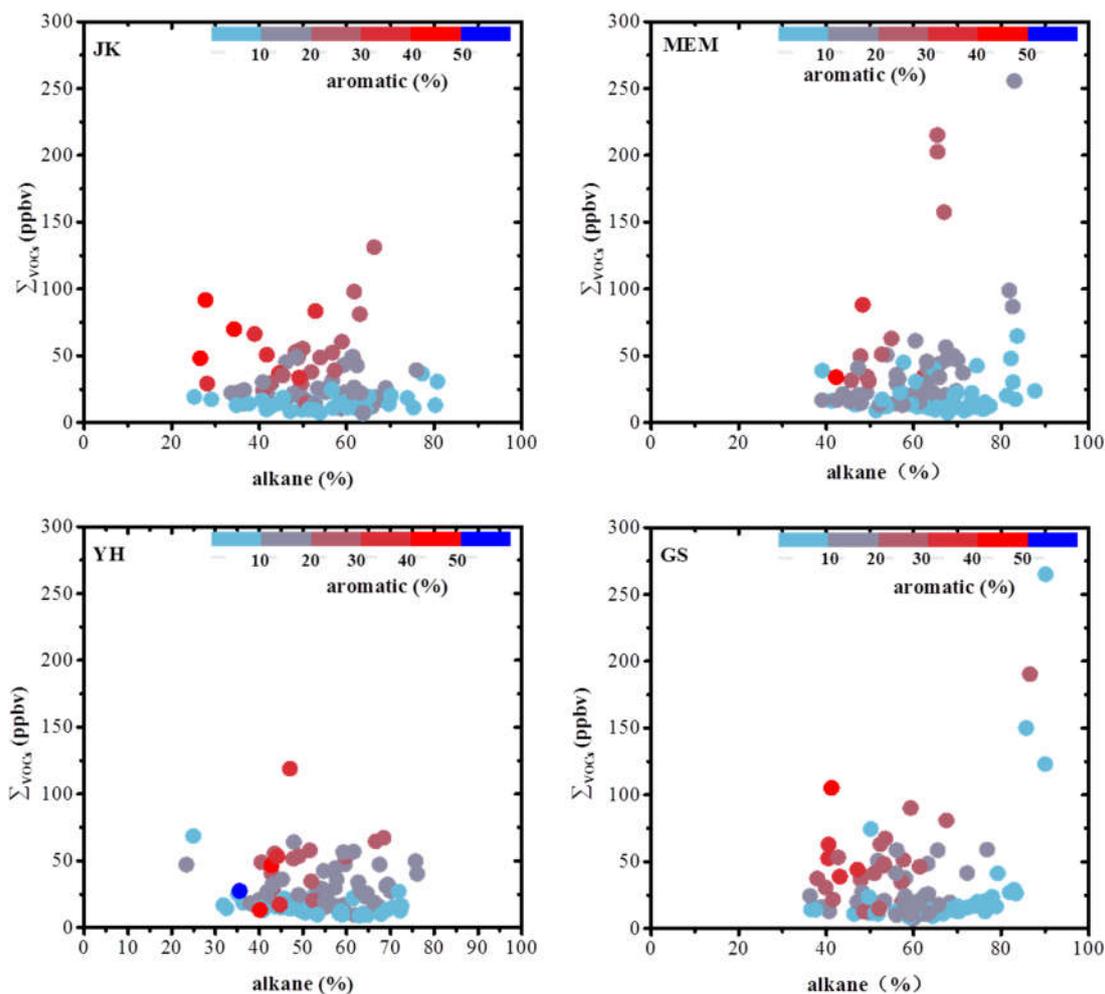
385 Fig.6 Temporal variations of mixing ratios of  $\Sigma_{\text{VOCs}}$ , NOx and O<sub>3</sub> at the four sites during the whole  
 386 sampling period, in which  $\Sigma_{\text{VOCs-07}}$  stands for the concentration level of  $\Sigma_{\text{VOCs}}$  observed at 07:00  
 387 LT, and  $\Sigma_{\text{VOCs-14}}$  was that observed at 14:00 LT.

388 **Comment 49:**

389 I cannot see this in Fig. 3

390 **Response:**

391 We have presented it in newly Fig. 7.



392

393 Fig. 7 The relationship between mixing ratio of  $\Sigma_{\text{VOCs}}$  and the composition of alkane, the data  
 394 points were color coded with the composition of aromatic.

395 **Comment 50:**

396 Not easily observed in Fig.3

397 **Response:**

398 We have modified the figure and presented in newly Fig. 7.

399 **Comment 51:**

400 Why? Can you show this?

401 **Response:**

402 The simultaneous increases in concentration of  $\text{SO}_2$ , CO and  $\text{NO}_x$  represent the  
 403 characters of potential combustion source, which could be caused by the nearby  
 404 thermal power plant.

405 **Comment 52:**

406 (Reason for disturbance?)

407 **Response:**

408 During the sampling period, the building where we conducted the sampling had  
409 painting activities during June, 2017.

410 **Comment 53:**

411 Wind direction will confirm this

412 **Response:**

413 The wind direction was added as:

414 *"The results support the possible impact from a gas-fueled power plant located*  
415 *about 1 km southwest of the site (~18% of prevailing western wind at GS during*  
416 *May to September)."*

417 **Comment 54:**

418 Combine with next paragraph

419 **Response:**

420 We think it is not so appropriate to combine the two paragraphs. The discussion of  
421 next paragraph is on alkyne.

422 **Comment 55:**

423 Give a reference for acetylene associated with biomass burning.

424 **Response:**

425 *A reference of Zhu et al, 2016 has been added.*

426 *"Zhu, Y., Yang, L., Chen, J., Wang, X., Xue, L., Sui, X., Wen, L., Xu, C., Yao, L.,*  
427 *Zhang, J., Shao, M., Lu, S., and Wang, W.: Characteristics of ambient volatile*  
428 *organic compounds and the influence of biomass burning at a rural site in*  
429 *Northern China during summer 2013, Atmospheric Environment, 124, 156-165,*  
430 *10.1016/j.atmosenv.2015.08.097, 2016."*

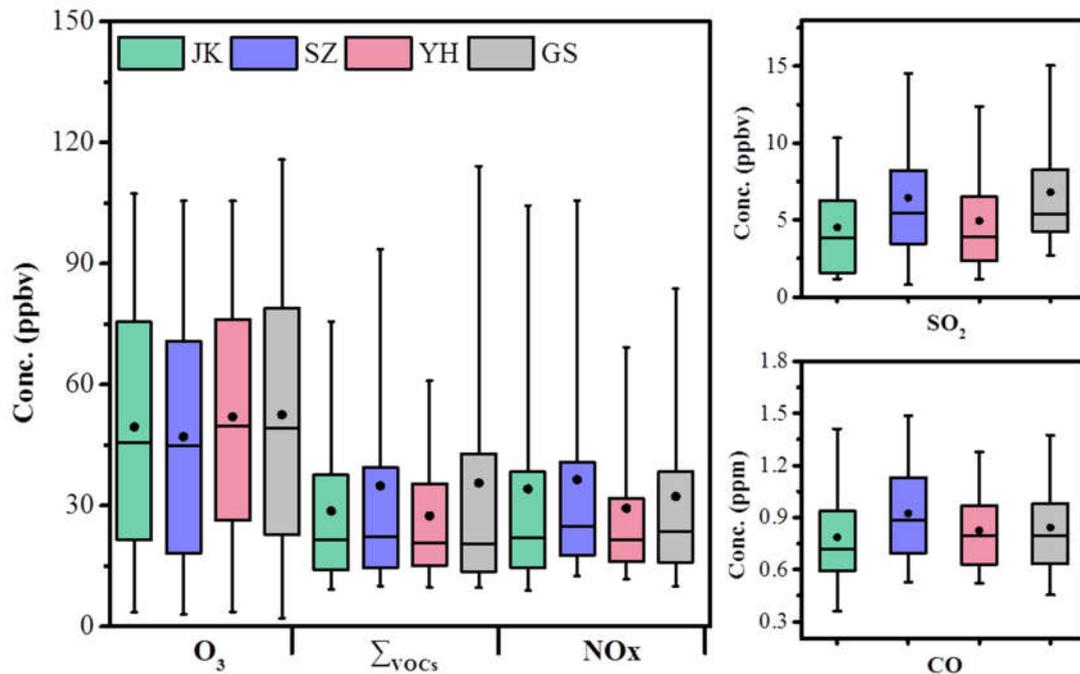
431 **Comment 56:**

432 Instead of Table 4, rather presented a figure with statistical distributions of total  
433 VOCs, SO<sub>2</sub>, O<sub>3</sub> etc measured at each site. This will greatly assist in discussion.  
434 Paragraph in Section 3.1 where different monthly total VOC concentrations at each of

435 the sites are explained with the influence of wind direction and -speed will also better  
436 fit within the discussion on spatial variations. The structure of this section must also  
437 be improved.

438 **Response:**

439 The original table has been replaced by Fig. 9.



440

441 Fig. 9 The distribution of concentration point on O<sub>3</sub>, ΣVOCs, NO<sub>x</sub>, SO<sub>2</sub> and CO at each site, the  
442 range of the box was 25%-75%, the black line in the box stands for median level, the black dot  
443 represent the average level, the range of whisker was 5-95%.

444 While the paragraph in Section 3.1 was more focus on meteorological factors, so it  
445 has not been moved to this section

446 **Comment 57:**

447 Not really. Differences are marginal

448 **Response:**

449 Yes, we agree that the difference is marginal. However, it is true that GS and JK had  
450 higher absolute values, so we have changed it to “*slightly higher*” in the text.

451 **Comment 58:**

452 This is not true. Differences are marginal

453 **Response:**

454 Yes, the difference is marginal. We have thus changed to

455 *“Additionally, the air pollutants related to the combustion processes, such as SO<sub>2</sub>*  
456 *and CO, were more abundant, though marginal, in western area of Zhengzhou*  
457 *(GS and MEM) (Fig.9).”.*

458 **Comment 59:**

459 Again, marginal differences between sites

460 **Response:**

461 The sentence has been rewritten as

462 *“Under high levels of VOCs and sufficient supply of NO<sub>x</sub>, the highest average*  
463 *mixing ratio of O<sub>3</sub> was observed at GS, followed by YH where even with the*  
464 *lowest VOCs and NO<sub>x</sub>, indicating that there are multiple factors, rather than the*  
465 *absolute concentrations, contributed to the O<sub>3</sub> formation at YH.”*

466 **Comment 60:**

467 Inconsequential statement from observation

468 **Response:**

469 The point has been deleted

470 **Comment 61:**

471 This sentence does not fit within the flow of the content

472 **Response:**

473 For in June, the O<sub>3</sub> concentration often exceeded the national standard level of 80  
474 ppbv, meaning severe air pollution caused by ozone during this period, in this section  
475 we focus on the period to discuss the relationship between VOCs and O<sub>3</sub> as a result.

476 **Comment 62:**

477 Small differences. Cannot really make this statement.

478 **Response:**

479 We do agree this. The sentence has been thus rewritten as

480 *"The weight percentage of aromatics (15.62±12.06%) at GS was higher than*  
481 *those at other sites as well, indicating that the painting and other renovation*  
482 *activities at GS was potentially an important factor for its high O<sub>3</sub> level in June.”*

483 **Comment 63:**

484 How is this substantiated?

485 **Response:**

486 Solvent usage is an important source of aromatics. Considering the renovation activity  
487 in June at GS, the higher aromatic composition should be caused by the renovation.  
488 According to aromatics with high reactivity, we thus suspect that the higher ozone  
489 level in June at GS was associated with the renovation activity

490 **Comment 64:**

491 O<sub>3</sub> levels were only higher at GS

492 **Response:**

493 Thank for the pointing out this. The statement has been revised as:

494 *"The higher level of O<sub>3</sub> at GS was accompanied with the higher  $\Sigma_{VOCs}$*   
495 *(39.29±25.37ppbv)."*

496 **Comment 65:**

497 Bad writing

498 **Response:**

499 The statement has been revised as:

500 *"Even though both the  $\Sigma_{VOCs}$  and specifically high O<sub>3</sub> formation potential*  
501 *compounds (such as alkenes and aromatics) at MEM were slightly higher than*  
502 *those at YH (Table 4), the O<sub>3</sub> concentration at MEM was not higher."*

503 **Comment 66:**

504 O<sub>3</sub> can only be formed from NO<sub>2</sub>.

505 **Response:**

506 We certainly recognize this. However, NO<sub>2</sub> was formed from NO, and NO could  
507 consume O<sub>3</sub>. Considering that ozone formation involved all the process mentioned  
508 above, we do think it is reasonable to address the NO<sub>x</sub> impact on ozone formation.

509 **Comment 67:**

510 In China? Give a reference please. Where is Hebei located in relation to Beijing?  
511 Sentences 311 - 315 another example of incoherent writing.

512 **Response:**

513 The statement has been revised as:

514 *"It is well known that many O<sub>3</sub> episodes were attributable not only to local*  
515 *sources but also to regional transports. For example, Streets et al. (2007)*  
516 *reported that with continuous southern winds, the O<sub>3</sub> level in Beijing was 20-30%*  
517 *contributed from its neighboring cities in Hebei. "*

518 **Comment 68:**

519 From Fig. 3 this surely does not look like the day on which O<sub>3</sub> peaks at all the sites in  
520 this study.

521 **Response:**

522 Yes, it is only happened at YH, and the content was revised accordingly in the text.

523 **Comment 69:**

524 VOCs are the important contributors to O<sub>3</sub> formation within a VOC-limited regime,  
525 i.e. very high NO<sub>x</sub>. I am sure that this is the case for the very polluted regions in  
526 China.

527 **Response:**

528 Thank you for the reminder. The evidence has been added as

529 *"On that day, the ratios of  $\Sigma_{VOCs}/NO_x$  at the four sites were all less than 6.5*  
530 *(ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that VOCs*  
531 *are the critical contributors to the formation of O<sub>3</sub> in Zhengzhou"*

532 **Comment 70:**

533 Fig. 4 is poorly introduced in the text and not sufficiently discussed.

534 **Response:**

535 The statement has rewritten as

536 *"The reductions in  $\Sigma_{VOCs}$  in the afternoons (around 14:00 LT) compared to*  
537 *mornings (around 07:00 LT) may have been caused from the uptake by O<sub>3</sub>*  
538 *formation, while the reduction of  $\Sigma_{VOCs}$  and active compounds (i.e.,*  
539 *aromatic+alkene) at 14:00 relative to 07:00, determined as 35% and 56%*  
540 *respectively, were the least at YH among the four sites (Fig. S4)."*

541 **Comment 71:**

542 You refer to aging in air masses.

543 **Response:**

544 Yes, this can be confirmed with its high E/X ratio (0.91) at 14:00, while the ratio for  
545 fresh air usually scattered around 0.3.

546 **Comment 72:**

547 Therefore VOC-limited due to very high NO<sub>x</sub>

548 **Response:**

549 Yes, it is.

550 **Comment 73:**

551 The construction in this section must also be improved. The authors interchange  
552 between T/B ratios and T/B correlations, which are two totally different aspects. Both  
553 are indicative of source, but in different manner. T/B ratios can be related to source  
554 and aging.

555 This section also links to your source apportionment section.

556 **Response:**

557 Yes, it is exactly right. The original text may be obscure. The explanation has been  
558 improved as below:

559 *“In this study, the correlation between benzene and toluene was fairly well at all*  
560 *the sites ( $R^2=0.70-0.74$ ), except for YH ( $R^2=0.41$ ) (Fig.14), suggesting the similar*  
561 *sources for benzene and toluene at JK, MEM and GS, while more complex such*  
562 *as variable wind direction at YH. The average ratios of T/B were lied within the*  
563 *range of 1.64-2.29, which were scattered around the character ratio of 2 for*  
564 *vehicle exhaust, illustrating the significance of vehicle emissions at the four*  
565 *sites.”*

566 **Comment 74:**

567 Poorly written sentence

568 **Response:**

569 The statement has been rewritten as

570 *“Specifically, at JK, MEM and YH, most of T/B ratios were distributed between*  
571 *0.6 and 3, which were corresponding to character ratios for coal or biomass*  
572 *burning and industrial activities respectively. These reflected the mixture impacts*  
573 *from mobile source and coal/biomass burning at these three sites. However, more*  
574 *values were greater than 3 at GS, suggesting more frequent disturbance from*  
575 *industrial activities at this site.”*

576 **Comment 75:**

577 Increased regionally in view of temporal variations?? This deduction does not make  
578 sense.

579 **Response:**

580 The statement has been revised as

581 *” From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00*  
582 *LT (Fig.15). In fact, the reaction rate constant of toluene*  
583 *( $5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) with  $\bullet\text{OH}$  is much higher than that for benzene*  
584 *( $1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), representing more rapid consumption of toluene*  
585 *from photochemical reactions and thus resulting in lower T/B ratios at 14:00 LT.*  
586 *Besides, the emission strength of mobile source is often weaker at 14:00 LT,*  
587 *while the coal/biomass burning are increased due to more human activities. Both*  
588 *of the situations can be used to explain the lower T/B ratios observed at 14:00*  
589 *LT.”*

590 **Comment 76:**

591 Please do not confuse T/B ratio and T/B correlations here. T/B correlation is  
592 indicative of similar sources, while T/B ratio indicate sources and aging.

593 What does this mean/imply?

594 **Response:**

595 We agree with this point. The statement has been revised as

596 *“In this study, the correlation between benzene and toluene was fairly well at all*  
597 *the sites ( $R^2=0.70-0.74$ ), except for YH ( $R^2=0.41$ ) (Fig.14), suggesting the similar*  
598 *sources for benzene and toluene at JK, MEM and GS, while more complex such*  
599 *as variable wind direction at YH.”*

600 **Comment 77:**

601 One would start/begin the paragraph with these sentences to indicate to what sources  
602 specific ratios of these two compounds can be related to and then you discuss your  
603 observed ratios in your study and relate them to these typical ratios. Another example  
604 of incoherent writing.

605 **Response:**

606 Newly lines 374-380 have been revised accordingly.

607 **Comment 78:**

608 Toluene is an aromatic species and NOT an alkene.

609 **Response:**

610 Yes, we truly know this. The original statement may lead confusion and it has been  
611 revised as

612 *“For the individual species, the top 10 most contributors in OFP included*  
613 *ethylene, isoprene, m,p-xylene, toluene, propylene, acetylene, n-butane,*  
614 *i-pentane and propane.”*

615 **Comment 79:**

616 What type of combustion? This paragraph is poorly structured and must be improved.

617 **Response:**

618 Based on analysis conducted in other sections, we inferred the combustion source as  
619 vehicle emissions and biofuel burning. and the paragraph was restructured.

620 **Comment 80:**

621 The VOC/NO<sub>x</sub> ratio is used to establish whether a region is VOC or NO<sub>x</sub> limited.  
622 Here you must indicate whether VOCs or NO<sub>x</sub> are the limiting factors.

623 High VOC/NO<sub>x</sub> ratio indicative of region being NO<sub>x</sub> limited. In such a region NO<sub>x</sub>  
624 determine O<sub>3</sub> levels and not VOCs. Higher ratios only indicate high VOCs in relation  
625 to NO<sub>x</sub>. If there is not enough NO<sub>x</sub>, O<sub>3</sub> will not form, since it can only form from  
626 NO<sub>2</sub>. Therefore to say that higher O<sub>3</sub> correspond to higher VOC/NO<sub>x</sub> ratios does not  
627 make sense. More VOCs in the absence of NO<sub>x</sub> will not form O<sub>3</sub>. Therefore, I think  
628 at your site you have high NO<sub>x</sub>, which is the only scenario where O<sub>3</sub> formation is  
629 considered VOC sensitive.

630 **Response:**

631 We have added a new section 3.4, which is mainly discussed the variation of  
632 VOCs/NO<sub>x</sub> ratios.

633 *“The VOCs/NO<sub>x</sub> ratio is often used to distinguish a region is either VOCs or NO<sub>x</sub>*  
634 *limited in O<sub>3</sub> formation. According to the general case, the area was loaded in*  
635 *VOC-sensitive regimes when VOCs/NO<sub>x</sub> ratios were lower than 10 in the*  
636 *morning; and it would be on NO<sub>x</sub>-sensitive regime when VOCs/NO<sub>x</sub> ratios were*  
637 *greater than 20 (Sillman, 1999;Hanna et al., 1996). In this study, the mean value*  
638 *of VOCs /NO<sub>x</sub> (ppbC/ppbv) were below 5 at all four sites (Fig.10), and 75% of*  
639 *the data points were < 6, indicating that the O<sub>3</sub> formation was sensitive to VOCs*

640 *in Zhengzhou, and the reductions on the emissions of VOCs will be benefit for O<sub>3</sub>*  
641 *alleviation.*

642 *The VOCs /NO<sub>x</sub> showed differences among the four sites (Fig. 10), with the lowest*  
643 *value at MEM (~3.8) and the highest value at JK (~4.7). The distributions*  
644 *demonstrated that the production of O<sub>3</sub> at MEM was more sensitive to VOCs than*  
645 *JK due to presence of emission from thermal-power plant. Meanwhile,*  
646 *approximately 14% of the VOCs /NO<sub>x</sub> ratios of >8.0 were found in the*  
647 *NO<sub>x</sub>-limited site of JK, potentially resulting from higher VOCs or lower NO<sub>x</sub>*  
648 *emissions than other sites. Both of the mixing ratios and the statistical data*  
649 *showed higher levels of VOCs (with lower NO<sub>x</sub>) at GS, where only ~4% of the*  
650 *ratios of > 8 was observed, indicating that there must be other factors*  
651 *(unresolved in this study) impacted the variation of O<sub>3</sub> formation regimes.*

652 *From the daily variations of VOCs /NO<sub>x</sub> ratios (Fig. 10), higher values were*  
653 *observed at 14:00 LT than 07:00 LT at the four sites, well correlated with less*  
654 *vehicle emissions or more consumption paths for NO<sub>x</sub> with stronger light*  
655 *intensity. The increment of VOCs /NO<sub>x</sub> at 14:00 LT was more obvious at JK and*  
656 *GS, suggesting that more emission sources of VOCs at daytime, and resulting the*  
657 *O<sub>3</sub> formation system shifting to the transition area in the afternoon.*

658 *Many researches showed that the O<sub>3</sub> formation depends not only on the*  
659 *abundances of precursors (mainly VOCs and NO<sub>x</sub>) and also VOCs to NO<sub>x</sub> ratio*  
660 *(Pollack et al., 2013). In this research, the mixing ratio of O<sub>3</sub> at 14:00 LT*  
661 *presented a slightly positive trend (p<0.05) with the uplift of VOCs /NO<sub>x</sub> at JK*  
662 *(Fig. 11), consistent to the results observed at the megacity of Shanghai (Gao et*  
663 *al., 2017), where the O<sub>3</sub> formation was more sensitive to NO<sub>x</sub> when high O<sub>3</sub> levels*  
664 *were observed. This can be attributed to the increased O<sub>3</sub> production efficiency at*  
665 *high VOCs /NO<sub>x</sub>. There were no discernible trends at other sites, possibly due to*  
666 *the counteraction imposed by other uncertain factors.”*

667 **Comment 81:**

668 Similar to all other sections, this section can also be better written and structured  
669 (section 3.7).

670 **Response:**

671 This section has been re-structured in other parts.

672 **Comment 82:**

673 This section must also be improved. I also suggest to combine this with Section 3.1  
674 where differences in VOC concentrations for different months are discussed and

675 explained with wind direction and -speed. Therefore combine local and long-range  
676 transport. Also see general comment at Section 3.1 to include all this in Section 3.2.

677 **Response:**

678 It has been incorporated in section 3.1 and 3.2

679 **Comment 83:**

680 Very busy figure with too much information.

681 **Response:**

682 Suggestion taken. The original figures have been decomposed as Fig.13 and Fig.14.

683 **Comment 84:**

684 Please describe this better. All the figures are small. You mean "smaller" figures.

685 **Response:**

686 Thanks for the reminder. The vertical axis in every small figure represents the mixing  
687 ratio of toluene (ppbv), while the horizontal axis stands for benzene level (ppbv).

688

## 689 **Comment & response #2**

### 690 **Overview**

691 1. The manuscript requires extensive English language editing. It is not currently  
692 suitable for publication as there are too many places in which weaknesses in English  
693 make it unclear, ambiguous or difficult to understand the point the authors are  
694 making;

695

### 696 **Response:**

697

698 Sorry and thanks for suggestion. The manuscript has been reviewed by a native  
699 English speaker.

700

701 2. The abbreviation “PAMS” stands for Photochemical Assessment Monitoring  
702 Stations, referring to the locations at which VOC sampling and monitoring are  
703 conducted. It does not refer to the compounds sampled, for which “VOC” (or VOCp  
704 to distinguish those isolated here from the generic term) should be used.

705

### 706 **Response:**

707

708 We had used the term of PAMS for the representation of 57 critical ozone precursors,  
709 which are defined in the Photochemical Assessment Monitoring Stations. The term  
710 has been replaced in the revised manuscript.

711

712 3. My chief concern with this work is the limited (and potentially biased) nature of the  
713 data collected, as outlined above. This precludes the authors from reaching robust  
714 conclusions regarding meteorological drivers of ozone, inter-annual variability, and  
715 the precise cause of the observed increase in ozone in Zhengzhou City, as well as  
716 preventing them from being able to offer clear policy advice regarding emissions  
717 controls.

718

### 719 **Response:**

720

721 We did understand the concern from the reviewer. However, the study was conducted  
722 for five months in a year, covering the entire period troubled with ozone pollution.  
723 The scale of sampling campaign is much systematic and larger than any local research  
724 conducted in the central China. Certainly, continuous monitoring and extension of the  
725 work is necessary while the most efficient policy is being established for emission  
726 controls.

727

728 4. The authors need to give far more detail of the prevailing meteorology in  
729 Zhengzhou, at the very least the typical intra- and inter-annual variability to put the  
730 sampling time period into context.

731

732 **Response:**

733

734 The manuscript has been revised according to both reviewers' suggestion. The  
735 discussion on meteorology has been improved.

736

737 5. Some of the analysis techniques used have associated limitations which the authors  
738 do not discuss. For example, PMF analysis requires that the inputs (here the  
739 concentrations) are independent when that will not be the case here. PMF is a  
740 well-established and accepted method for source apportionment analysis but the  
741 authors should be clear about its limitations. Likewise, the actual rate of ozone  
742 formation from any specific VOC is strongly dependent on both chemical and  
743 meteorological conditions and can only be reliably estimated using detailed  
744 atmospheric chemistry models. While ozone formation potentials based on constant  
745 maximal incremental reactivity (MIR) ratios are a useful indicator of which VOCs  
746 may be most important to control they are only an indicator. Again the authors need to  
747 be clear about this. The following reference may be of use: "Photochemical ozone  
748 creation potentials for organic compounds in northwest Europe calculated with a  
749 master chemical mechanism". Derwent, R.G. et al., 1998; doi:  
750 10.1016/S1352-2310(98)00053-3

751

752 **Response:**

753

754 The discussions on source apportionment and reactivity of VOCs in ozone formation  
755 have been improved. Please refer to those details for the related sections on the  
756 point-to-point responses.

757

758 6. I cannot over-emphasize the importance of wind direction to the analyses presented  
759 here. It is critical in terms of both the transport of longer-lived and secondary  
760 pollutants and the local production. Local production is affected by meteorology  
761 which is often synoptic in scale and therefore correlated with windspeed and direction.  
762 Meteorological conditions will affect both photochemical efficiency and pollutant  
763 source strengths. This importance should be reflected in both the text and the figures.  
764 The back-trajectories tucked away right at the end as Fig. 10 should be incorporated  
765 into Fig. 1 and presented in the text ahead of the analysis of possible local production  
766 sources.

767

768 **Response:**

769

770 As the same as point (4), we have interpreted the influences on meteorological  
771 conditions including wind direction and speed in the explanation of local and regional  
772 transfer of pollutants.

773

774 7. Following on from this, there is also a real need for a windrose plot showing met  
775 conditions of importance (from the text = T, RH, although radiation would also be

776 useful) and concentrations of the various pollutants for each of the 4 locations and  
777 possibly also split out by month. While I appreciate the authors have attempted to  
778 highlight the contribution of wind direction (and speed) in Fig. 4 and through various  
779 color-coding in Fig. 7 I don't think these give the clear oversight required given the  
780 key role winds play. See e.g.  
781 <http://www.openair-project.org/examples/BivariatePolarPlots.aspx> or  
782 <http://www.openair-project.org/examples/windpollutionroses.aspx> for open source  
783 visualization tools

784

785 **Response:**

786

787 [Thanks for the appreciation on our work and we have revised the related figures](#)  
788 [accordingly.](#)

789

790 8. As the manuscript stands, the SI seems rather unnecessary as it consists of a single  
791 plot. I have however made several recommendations below regarding moving  
792 material out of main text

793

794 **Response:**

795

796 [Thanks for the reviewer's suggestion and comments on our submitted manuscript. We](#)  
797 [have made point-to-point responses to each comment as below in detail.](#)

798

799 **Introduction:**

800

801 **Comment 1**

802

803 This section is particularly difficult to follow. It is hard to work out which parts refer  
804 to previous work and how relevant these are. The authors do not explain how the  
805 different regimes reported from e.g. Los Angeles and SE USA relate to Zhengzhou.

806

807 **Response:**

808

809 [The statement has been revised. The original aim of the statement was to support the](#)  
810 [importance of VOCs studies in different regions. This has been deleted according to](#)  
811 [suggestion.](#)

812

813 **Comment 2**

814

815 Many of the references are not the most appropriate to the point the authors appear to  
816 be making. For example, Capps et al applied a methodology that was developed  
817 previously by e.g. Carter et al., Derwent et al., etc.

818

819 **Response:**

820

821 We have made more clarification and checked the citations. The reference of Capps et  
822 al was replaced by Carter et al.(1994) as suggested.

823

824 *“Carter, W. Development of Ozone Reactivity Scales for Volatile Organic*  
825 *Compounds; J. Air & Waste Manage. Assoc. 1994, 44, 881-899. “*

826

827 **Comment 3**

828 L81: “one of the most polluted cities” where? In China? Asia? Globally?

829

830 **Response:**

831

832 The statement has been revised as:

833

834 *“With the rapid growth of industrial activities, as well as increased vehicle*  
835 *emissions and fuel combustions, air quality in Zhengzhou has notoriously*  
836 *deteriorated. The Air quality index (AQI) for 65% of the days in 2013 exceeded*  
837 *the allowable limits of 100 established by the Air Quality Guideline. ” .*

838

839 **Comment 4**

840 L81-2: “its air quality exceeds the allowable limits set by Air Quality Guidelines” -  
841 specifically which pollutants exceeded the limits and what are the limits

842

843 **Response:**

844

845 The limits are referred to the guideline of air quality index (AQI) in China. In 2012,  
846 the Chinese Ministry of Environmental Protection (CMEP) issued the Ambient Air  
847 Quality Index (AQI) Technical Provisions (Trial) (HJ 633 - 2012) on the basis of the  
848 United States Environmental Protection Agency (U.S.EPA) AQI objective, and it was  
849 implemented as the Chinese Ambient Air Quality Standard (CAAQS) (GB  
850 3095-2012). The AQI level is determined by the concentrations of six criteria  
851 pollutants including SO<sub>2</sub>, NO<sub>2</sub>, CO, O<sub>3</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>. Basically, the AQI acts as a  
852 guideline for local government to inform the public and to take proper health  
853 protection measures.

854

855 **Experimental:**

856

857 **Sampling site:**

858

859 **Comment 5**

860 What was the sampling duration and flow rate?

861

862 **Response:**

863

864 The description has been revised as

865

866 *“Grab samples were collected minute using 3.2 L stainless-steel canisters (Entech*  
867 *Instrument, Inc., Simi Valley, CA, USA), which were pre-cleaned with high purity*  
868 *nitrogen and pressurized to 20 psi.”.*

869

870 **Comment 6**

871 Why did the authors select 07:00 and 14:00 as the two sampling times? How do these  
872 relate with rush hour? Or mealtimes? Or the working day?

873

874 **Response 6**

875

876 The statement has been revised as

877

878 *“Two samples, one collected at 07:00 with increasing of human activities and*  
879 *another one collected at 14:00 with well-mixed of ambient air, were obtained on*  
880 *each sampling day.”.*

881

882 **Chemical analysis:**

883

884 **Comment 7**

885 What was the specific compound mix in each of the three standard gases? There are  
886 issues regarding extrapolating area: concentration scaling factors from 1 compound to  
887 another even for structurally similar compounds and those with similar retention times  
888 (see e.g. Ruiz-Hernandez et al., 2018; doi:10.1186/s13007-018-0335-2))

889

890 **Response:**

891

892 The 57 VOCs (defined as the most critical contributors for ozone) discussed in this  
893 paper were quantified with the PAMS standard gas (1 ppm; Spectra Gases Inc, NJ,  
894 USA) containing 28 alkanes, 11 alkenes, acetylene and 17 aromatics. The other two  
895 standard gases were used to quantify halocarbons and oxygenated VOCs, but they  
896 have not been discussed in this manuscript. In order to avoid confusion, the  
897 information for the two standard gases has been removed. The extrapolating method  
898 has not been used. The co-eluted compounds of m-xylene and p-xylene were reported  
899 as m,p-xylene.

900

901 **QA/QC:**

902

903 **Comment 8**

904 This text could be moved to the SI if it is retained

905

906 **Response:**

907

908 Suggestion taken. The texts have been moved to SI.

909

910 **PMF:**

911

912 **Comment 9**

913 The authors go into far more detail of the specific equations (which are a standard  
914 technique) than is necessary in the main text. I suggest that the mathematical details  
915 of PMF are moved to the SI and the authors give more information regarding  
916 precisely how it was applied to their data.

917 The authors also need to include a statement regarding the limitations of applying  
918 PMF here.

919

920 **Response:**

921

922 Thanks for the suggestion. The mathematical details of PMF were moved to the SI,  
923 and the content in Section 2.3 has been rewritten.

924

925 **Results and discussions**

926

927 **Mixing ratios and meteorological variations:**

928

929 **Comment 10**

930 “VOCs” not “PAMS” Are the reported meteorological data over the entire month or  
931 just the 10 days each month when the sampling was conducted?

932

933 **Response:**

934

935 The term of “PAMS” has been replaced with “VOCs” in the text. The meteorological  
936 data were covered the 10 sampling days in each month.

937

938 **Comment 11**

939 Are the average VOC concentrations for all samples taken in that month, i.e.  
940 combining the 07:00 and 14:00 sampling times? This would be misleading as it would  
941 be expected that values and sources differ markedly between those two times of day.

942

943 **Response:**

944

945 Yes, the average concentrations represent the values from two sections (i.e., 07:00 and  
946 14:00) for each sampling day.

947

948 We do understand the concern about the variations of concentrations and contributions  
949 of the sources from time to time. There were many factors impacted the VOCs levels  
950 and composition indeed, while in this study we focus on the impacts from  
951 meteorological conditions in different month. Therefore, we have depicted the case by

952 the statement as

953

954 *“This can be attributed to numerous factors that will be explored later in the*  
955 *paper. Besides the emission sources (to be discussed in Section 3.2), the impacts*  
956 *controlled by meteorological conditions should not be ignored as well”.*

957

958 And, the diurnal variations have been discussed in other sections.

959

960 **Comment 12**

961 The large variability (reported standard deviations and month-to-month differences)  
962 indicate the clear need for sampling to continue over a much longer time period,  
963 taking in different times of day and for a number of years.

964

965 **Response:**

966

967 The objective of this study is to illustrate the characteristics of VOCs during the high  
968 ozone level period in a year. The sampling has been conducted for five months in a  
969 year, when were sufficiently representative.

970

971 **Comment 13**

972 L199: “more accumulated at GS”? I don’t understand what point the authors are  
973 making here. Do they refer to higher concentrations? Greater influence of transported  
974 pollution?

975

976 **Response:**

977

978 The sentence has been revised as

979

980 *“The average wind speed at GS ( $0.74\pm 0.33\text{ m s}^{-1}$ ) was lower than that at MEM*  
981 *( $1.84\pm 0.94\text{ m s}^{-1}$ ) and YH ( $0.97\pm 0.36\text{ m s}^{-1}$ ) (Table 3), indicating poor dispersion*  
982 *conditions at GS. The air pollutants emitted from MEM and YH were more liable*  
983 *resulting in a higher level of  $\Sigma_{\text{VOCs}}$  at GS in June.”*

984

985 **Comment 14**

986 L205: Likewise I don’t understand what the authors mean by “topographical effect”

987

988 **Response:**

989

990 Topographical effect is referred to a geographical factor impacted the distribution of  
991 VOCs. In this study, the sites of GS and MEM were located at the western part of  
992 Zhengzhou, while JK and YH were belong to the eastern part. Since the VOCs levels  
993 gradually increased from east to west, we have thus suspected that the concentrations  
994 of VOCs could be correlated with the topography.

995

996 **Comment 15**  
997 The authors have used PMF to identify source sectors and present the findings of this  
998 analysis in section 3.6. what is presented here is speculation which is entirely  
999 superfluous given they have used PMF later.

1000

1001 **Response:**

1002

1003 Suggestion taken. The paragraph has been revised as

1004

1005 *“The C<sub>2</sub> - C<sub>5</sub> alkanes, acetylene, ethylene, toluene and benzene were the most*  
1006 *abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene*  
1007 *varied within a wide range at each site, because of its universal emission sources*  
1008 *(e.g., vehicle exhaust emissions and solvent usage) (Wang et al., 2014; Barletta et*  
1009 *al., 2005). These chemicals contributed >60% for ΣVOCs at each site,*  
1010 *illustrating strong combustion-related sources in Zhengzhou.”*

1011

1012 **Comment 16**

1013 It would seem to me to make more sense for the authors to discuss likely influences  
1014 from long-range transport of pollutants (i.e. HYSPLIT back-trajectory analyses here  
1015 shown in Section 3.7) BEFORE considering local sources.

1016

1017 **Response:**

1018

1019 Thanks for the suggestion. This has been moved to Section 3.1.

1020

1021 **Comment 17**

1022 L208: The authors describe the results as showing “the general consistency of  
1023 pollution sources in the region” but the large variability in the reported averages do  
1024 not appear to suggest that.

1025

1026 **Response:**

1027

1028 Even though the concentrations were variable, the compositions of major compounds  
1029 were similar at every site. Therefore, we do conclude that there were consistent  
1030 emission sources for each site.

1031

1032 **Comment 18**

1033 L221-222: The authors have not convincingly demonstrated this in their presented  
1034 results.

1035

1036 **Response:**

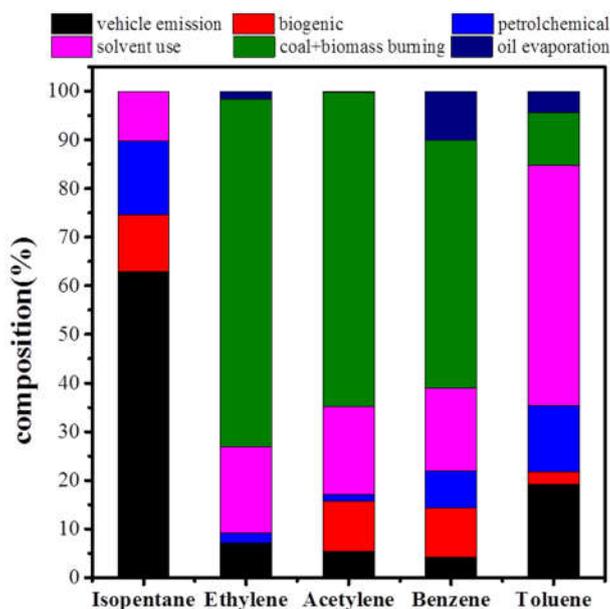
1037

1038 The paragraph has been revised as

1039

1040 “The C<sub>2</sub> - C<sub>5</sub> alkanes, acetylene, ethylene, toluene and benzene were the most  
1041 abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene  
1042 varied within a wide range at each site, because of its universal emission sources  
1043 (e.g., vehicle exhaust emissions and solvent usage) (Wang et al., 2014; Barletta et  
1044 al., 2005). These chemicals contributed >60% for ΣVOCs at each site, illustrating  
1045 strong combustion-related sources in Zhengzhou”

1046  
1047  
1048 According to results calculated by PMF, except for toluene in which solvent use  
1049 contributed more about 50%, these compounds were mainly originated from vehicle  
1050 and coal/biomass burning,



1051  
1052 *Fig. Major emission sources of abundant compounds apportioned by PMF.*

1053  
1054 **Comment 19**

1055 L231-232: Samples were taken at 07:00 and 14:00 only. The authors cannot make  
1056 general comments about morning and afternoon as they have not presented any data  
1057 to suggest that the conditions at 07:00 (14:00) persist throughout the morning  
1058 (afternoon)

1059  
1060 **Response:**

1061  
1062 The paragraph has been revised as,

1063  
1064 “Due to the variations of the planet boundary layer (PBL) height, solar radiation  
1065 and emission sources, the concentrations of VOCs displayed obvious differences  
1066 between morning and afternoon time (07:00LT and 14:00LT in this study).  
1067 Compared with morning period, the aromatic compounds showed lower  
1068 compositions at 14:00 LT (Fig. 5), because of the increased planet boundary layer  
1069 and the active photochemical reactions, while alkenes always peaked in the 14:00

1070 *LT. According to the dataset, the increases in alkene compositions (~4.3% uplift)*  
1071 *were mainly due to higher contributions of isoprene (~1.4% at morning and 7.6%*  
1072 *in the afternoon), which was mainly emitted from biogenic sources and increased*  
1073 *exponentially with ambient temperature (Jiang et al., 2018)."*  
1074

1075 **Temporal variations:**

1076

1077 **Comment 20**

1078 L261: "wash-out" specifically refers to rain which I don't think is what the authors  
1079 mean.

1080

1081 **Response:**

1082

1083 The sentence has been revised as

1084

1085 *"The occurrences of precipitation and raining were also frequent in most areas of*  
1086 *China during summer, resulting in decreasing background level of air pollutants"*

1087

1088 **Comment 21**

1089 L276: "sharp changes in local emissions" - such as?

1090

1091 **Response:**

1092

1093 These could be resulted from the local emissions such as coal combustion and leakage  
1094 of compressed natural gas (CNG) or LPG. We have explained this case in the  
1095 following statements:

1096

1097 *"Specifically, at MEM, the distinctive increment was always accompanied with*  
1098 *obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were often*  
1099 *consistent during the sampling period, the direct gas evaporations should be*  
1100 *constant as well. Therefore, the simultaneous increased concentrations of SO<sub>2</sub>,*  
1101 *CO and NO<sub>x</sub> could illustrate the potential impacts from combustion sources, such*  
1102 *as emissions from nearby thermal power plant. At GS, the increase of Σ<sub>VOCs</sub> in*  
1103 *June was usually with extremely high levels of aromatics, due to the disturbance*  
1104 *from solvent use for building renovation during this period, and the abnormal*  
1105 *high levels of Σ<sub>VOCs</sub> in other months were related to the rising concentrations of*  
1106 *C<sub>3</sub>-C<sub>4</sub> alkanes, which were mainly originated from consumptions of compressed*  
1107 *natural gas (CNG) or LPG (Huang et al., 2015b). The results support the*  
1108 *possible impact from a gas-fueled power plant located about 1 km southwest of*  
1109 *the site (~18% of prevailing western wind at GS during May to September)."*

1110

1111 **Comment 22**

1112 L278-9: It is not clear how changes in T and RH lead the authors to conclude  
1113 combustion sources were enhanced.

1114

1115 **Response:**

1116

1117 Since the T and RH were often consistent under normal conditions, the contributions  
1118 from gas evaporation should be also constant. Therefore, the simultaneous change of  
1119 SO<sub>2</sub>, CO and NO<sub>x</sub> should be caused by the enhancement of combustion sources. In  
1120 order to avoid confusion, we have rewritten the statement as:

1121

1122 *“Specifically, at MEM, the distinctive increment was always accompanied with*  
1123 *obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were often*  
1124 *consistent during the sampling period, the direct gas evaporations should be*  
1125 *constant as well. Therefore, the simultaneous increased concentrations of SO<sub>2</sub>,*  
1126 *CO and NO<sub>x</sub> could illustrate the potential impacts from combustion sources, such*  
1127 *as emissions from nearby thermal power plant.”*

1128

1129 **Comment 23**

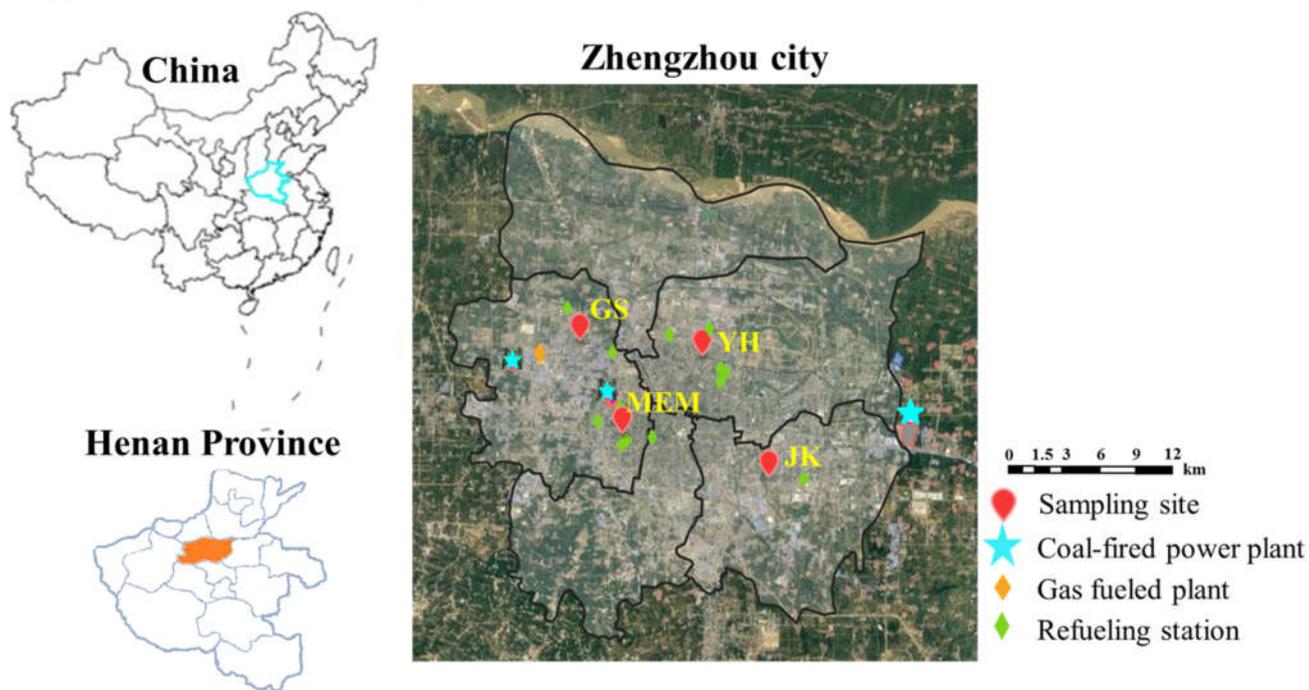
1130 It would be extremely helpful to have a more detailed map of Zhengzhou City  
1131 showing the 4 sites, key emission sources and prevailing wind.

1132

1133 **Response:**

1134

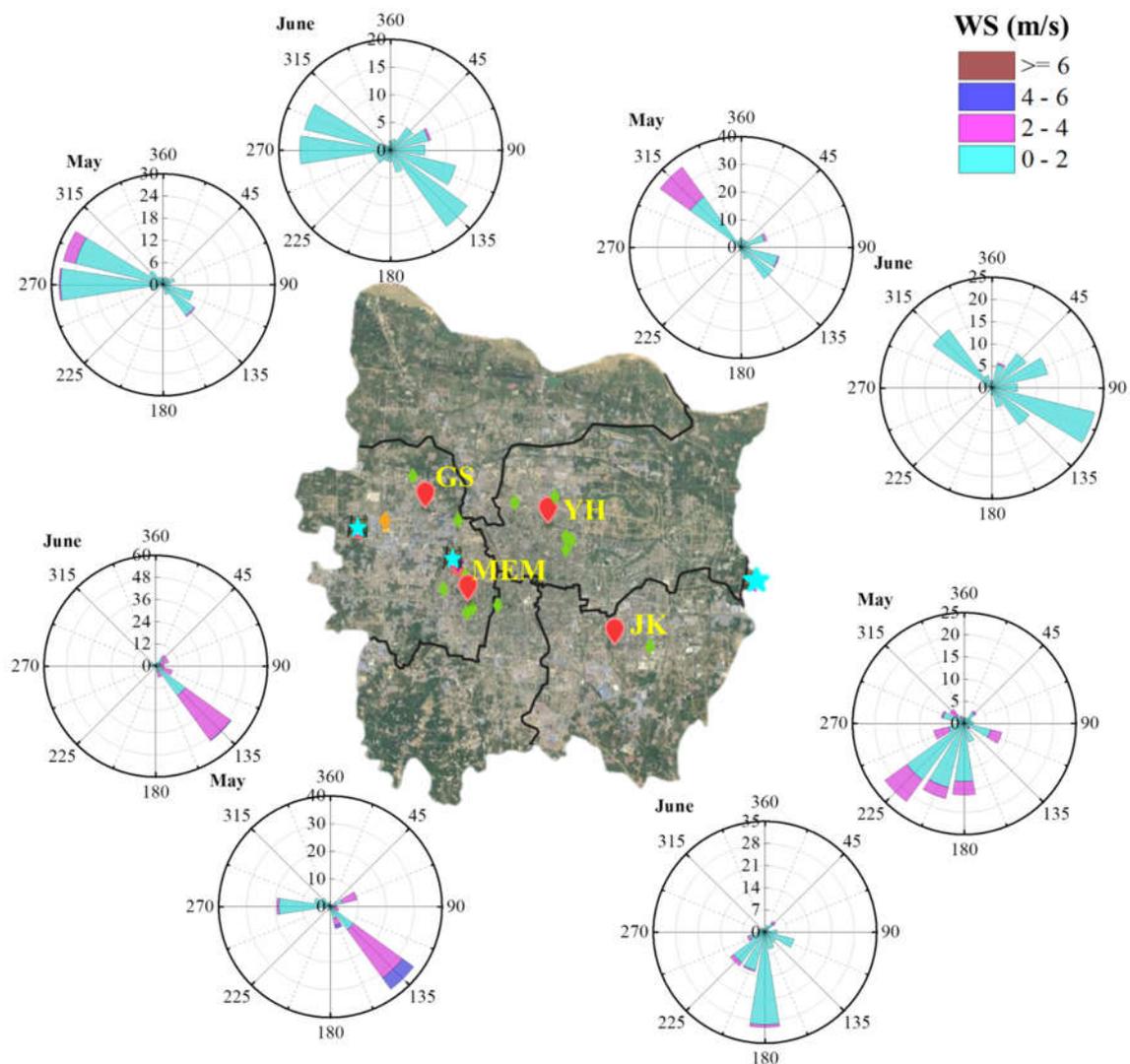
1135 Suggestion taken. The newly figure 1 and 4 have been revised as below:



1136

1137

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



1138

1139 Fig. 4 Wind rose of each site in May and June (the wind distribution in other three months were  
 1140 illustrated in Fig S2)

1141

1142 **Spatial variations:**

1143

1144 **Comment 24**

1145 L298-299:  $O_3$ - $NO_x$ -VOC interactions and reactions are always highly complex and  
 1146 non-linear, hence the development of ozone isopleths (see e.g. Silman, 1999)

1147

1148 **Response:**

1149

1150 Thanks for the recommend reference. There is a particular section (i.e, section 3.4) for  
 1151 discussion on the ratio of VOCs/ $NO_x$ .

1152

1153 **Comment 25**

1154 L300: Is this peak (i.e. hourly)  $O_3$  or 8-hour  $O_3$ ?

1155

1156 **Response:**

1157

1158 It is hourly average.

1159

1160 **Comment 26**

1161 L306-307: This sentence appears to contradict the results presented in L301-302.

1162

1163 **Response:**

1164

1165 There is no contradiction. The original L306-307 just pointed out that a reversible  
1166 observation on concentrations of O<sub>3</sub> and VOCs/OFP was seen at the two sites of  
1167 MEM and JH only. There are many different factors controlling the ozone formation.  
1168 The general trend is unchanged.

1169

1170 **Comment 27**

1171 L321-323: “when synoptic conditions were favorable” - yet in the abstract and  
1172 conclusions the authors state categorically that O<sub>3</sub> formation in Zhengzhou is  
1173 VOC-sensitive. If there is a caveat it should also be made clear in these other sections.

1174

1175 **Response:**

1176

1177 The discussion on ozone formation regime was presented in the newly Section 3.4.

1178

1179 **Comment 28**

1180 Please give typical T/B ratios for relevant sources.

1181

1182 **Response:**

1183

1184 We have provided the information as:

1185

1186 *“T/B is another efficient tool to differentiate between pollution sources, both the*  
1187 *tunnel studies and roadside researches indicated that T/B ratio varied within the*  
1188 *range of 1 - 2 when the atmosphere was heavily impacted by vehicle emissions*  
1189 *(Gentner et al., 2013;Tang et al., 2007;Huang et al., 2015b;Wang et al., 2002),*  
1190 *and when the ratio was less than 0.6, it may be due to other sources, such as coal*  
1191 *combustion and biomass burning (Tsai et al., 2003;Akagi et al., 2011). The*  
1192 *industrial activity would become more important when the value of T/B ratio is*  
1193 *higher than 3 (Zhang et al., 2015)”.*

1194

1195 **Comment 29**

1196 L334-336: Without knowing that the emission sources remained constant throughout  
1197 the time it is not possible to state definitively that the differences were due to  
1198 photochemistry.

1199

1200 **Response:**

1201 The relative statements have been revised as:

1202

1203 *“From the temporal respect, the T/B ratios at 14:00 LT were lower than at*  
1204 *07:00 LT (Fig.15). In fact, the reaction rate constant of toluene*  
1205 *( $5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) with  $\bullet\text{OH}$  is much higher than that for benzene*  
1206 *( $1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), representing more rapid consumption of toluene*  
1207 *from photochemical reactions and thus resulting in lower T/B ratios at 14:00 LT.*  
1208 *Besides, the emission strength of mobile source is often weaker at 14:00 LT, while*  
1209 *the coal/biomass burning are increased due to more human activities. Both of the*  
1210 *situations can be used to explain the lower T/B ratios observed at 14:00 LT. In*  
1211 *comparison with other months, higher T/B ratios were found more frequently in*  
1212 *September, potentially showing the more strengthen industrial activities during this*  
1213 *period.”*

1214

1215 **Comment 30**

1216 L336-337: The authors make many statements such as this without attempting to  
1217 explain why the observed difference may have occurred.

1218

1219 **Response:**

1220

1221 The incoherent statements have been deleted.

1222

1223 **Comment 31**

1224 L340-342: The absolute values should be reported before the  $R^2$  value.

1225

1226 **Response:**

1227

1228 Thanks for the reminder. The absolute values have been reported.

1229

1230 **Comment 32**

1231 L349: It would be possible to achieve these values with zero vehicle emissions but a  
1232 mixture of industrial and biomass burning emissions. Hence my previous comment  
1233 regarding the superfluity of this speculation given the authors have conducted PMF  
1234 for source-apportionment. But perhaps other pollutants monitored at the site also  
1235 provide insight into most likely sources?

1236

1237 **Response:**

1238

1239 The statement has been revised as

1240

1241 *“The average ratios of T/B were lied within the range of 1.64-2.29, which were*  
1242 *scattered around the character ratio of 2 for vehicle exhaust, illustrating the*  
1243 *significance of vehicle emissions at the four sites. Specifically, at JK, MEM and*

1244 *YH, most of T/B ratios were distributed between 0.6 and 3, which were*  
1245 *corresponding to character ratios for coal or biomass burning and industrial*  
1246 *activities respectively. These reflected the mixture impacts from mobile source*  
1247 *and coal/biomass burning at these three sites. However, more values were greater*  
1248 *than 3 at GS, suggesting more frequent disturbance from industrial activities at*  
1249 *this site.”*

1250

1251 **Comment 33**

1252 L355: How are the outliers (“abnormal values”) identified and removed?

1253

1254 **Response:**

1255

1256 The abnormal values defined as the data points did not distribute in the range of  
1257 5-95%, and thus were not taken into consideration in Section 3.5.

1258

1259 **Comment 35**

1260 L360-361: As previously noted, a windrose plot would be extremely helpful.

1261

1262 **Response:**

1263

1264 They have been now presented in newly Fig. 4 and Fig. S2.

1265

1266 **Comment 36**

1267 L360-361: This might be the prevailing wind, but what about the specific days  
1268 sampled?

1269

1270 **Response:**

1271

1272 The prevailing wind directions were often consistent with the wind directions on our  
1273 10 sampling days each month.

1274

1275 **Comment 37**

1276 i-pentane and n-pentane: Is this the ratio of i/n that the authors are reporting from  
1277 these previous studies?

1278

1279 **Response:**

1280

1281 In newly L374-380, the ratios from other studies have been added, and the values  
1282 observed in this study were presented in Fig.12.

1283

1284 **Comment 38**

1285 I would suggest that the authors reverse the order and discuss i/n ratios first as they  
1286 are NOT influenced by different reaction rates, and then discuss T/B ratios which are.

1287

1288 **Response:**  
1289 The relative statement has been moved to newly L374-391.

1290  
1291 **Reactive chemicals:**

1292  
1293 **Comment 39**  
1294 L389-390: As noted previously, there are caveats associated with OFPs. It is not just  
1295 the “reactivity” that matters when assessing the contribution of each individual  
1296 species to overall O<sub>3</sub> formation. Different mixtures of VOCs result in competition  
1297 between different species, leading to different relative yields, different reaction paths,  
1298 etc.

1299  
1300 **Response:**  
1301  
1302 The statements have been revised as:

1303  
1304 *“The reactivity of individual species was different, while mixtures of VOCs would*  
1305 *have competition the precursors between each other, leading to variations on*  
1306 *reaction paths and O<sub>3</sub> formation yields. Ozone formation potential (OFP) is a*  
1307 *useful tool to estimate maximum O<sub>3</sub> productions of each compound under*  
1308 *optimum conditions, from which the vital species in O<sub>3</sub> formation could be*  
1309 *identified.”*

1310  
1311 **Comment 40**  
1312 L392-395: The authors need to make it abundantly clear that this is an entirely  
1313 hypothetical potential (or maximum) possible O<sub>3</sub> formation for each compound in  
1314 isolation.

1315  
1316 **Response:**  
1317 The statement has been revised as:  
1318 *“Ozone formation potential (OFP) is a useful tool to estimate maximum O<sub>3</sub>*  
1319 *productions of each compound under optimum conditions, from which the vital*  
1320 *species in O<sub>3</sub> formation could be identified (Huang et al., 2017). The calculation*  
1321 *of OFP is based on mixing ratios and maximum incremental reactivity (MIR) of*  
1322 *individual compound, which are expressed in Eq. (4).”*

1323  
1324 **Comment 41**  
1325 L396: The authors should present their own results first and then put them into  
1326 context against previous studies. It’s not clear why they would expect relative  
1327 abundances and relative contributions to O<sub>3</sub> formation to be the same across different  
1328 regions with different sources and different meteorological conditions.

1329  
1330 **Response:**  
1331

1332 The paragraph has been rewritten as,

1333

1334 *“In Zhengzhou city, alkenes contribute most (55.91±14.17%) to the sum of OFP,*  
1335 *of which ethylene had the largest portion. The results is different with the*  
1336 *estimation based on emission inventories by Wu and Xie (2017), in which the*  
1337 *largest contributor of total OFP in North China Plain (NCP), YRD and PRD was*  
1338 *aromatics, reflecting that there was relatively less surface coating industries in*  
1339 *Zhengzhou.”*

1340

1341 The estimation was not considered meteorological conditions, and the provincial  
1342 emissions were calculated using equations:

$$E_t = \sum_{p=1}^N \left( \sum P_{m,n} \times VMT_{m,n} \times EF_{m,n} + \sum (1 - R_k) \times EF_{s,k} \times A_{s,k} \right) \times 10^{-12}$$

1343

1344 where  $E_t$  is the total VOC emission (Tg),  $P_{m,n}$  is the vehicular population of category  
1345  $m$  with emission standard  $n$  in province  $p$  ( $N = 31$ , including all of the provinces,  
1346 municipalities, and autonomous regions in mainland China),  $VMT_{m,n}$  and  $EF_{m,n}$  are  
1347 the corresponding annual average mileage (km) and emission factor (g/km),  
1348 respectively,  $R_k$  is the removal efficiency with technology  $k$ , and  $EF_{s,k}$  and  $A_{s,k}$  are the  
1349 corresponding emission factors and activity data for source  $s$  (except on-road  
1350 vehicles), respectively.

1351

1352 **Comment 42**

1353 L401: “fraction” rather than “composition”?

1354

1355 **Response:**

1356

1357 Yes, it should be “fraction”. The statement has been revised as:

1358

1359 *“the percentage of acetylene (4.51±0.34%) weighted in OFP was higher than*  
1360 *many other areas in China”*

1361

1362 **Comment 43**

1363 L410-411: Demonstrating the caution required in using and interpreting OFPs

1364

1365 **Response:**

1366

1367 Thanks for the reminder. The statement has been revised as,

1368

1369 *“Under low RHs and high T and OFP (88.13±30.32 ppbv), the O<sub>3</sub> level at YH*  
1370 *was unexpectedly lower than that at MEM on sunny days. Since the OFP was*

1371 *estimated with the assumption of reactions that proceeded under optimum*  
1372 *conditions, the above phenomenon reflected there were unsatisfied O<sub>3</sub> formation*  
1373 *conditions at YH.”*

1374

1375 **Comment 44**

1376 L414: And/or increased the importance of local versus long-distance sources.

1377

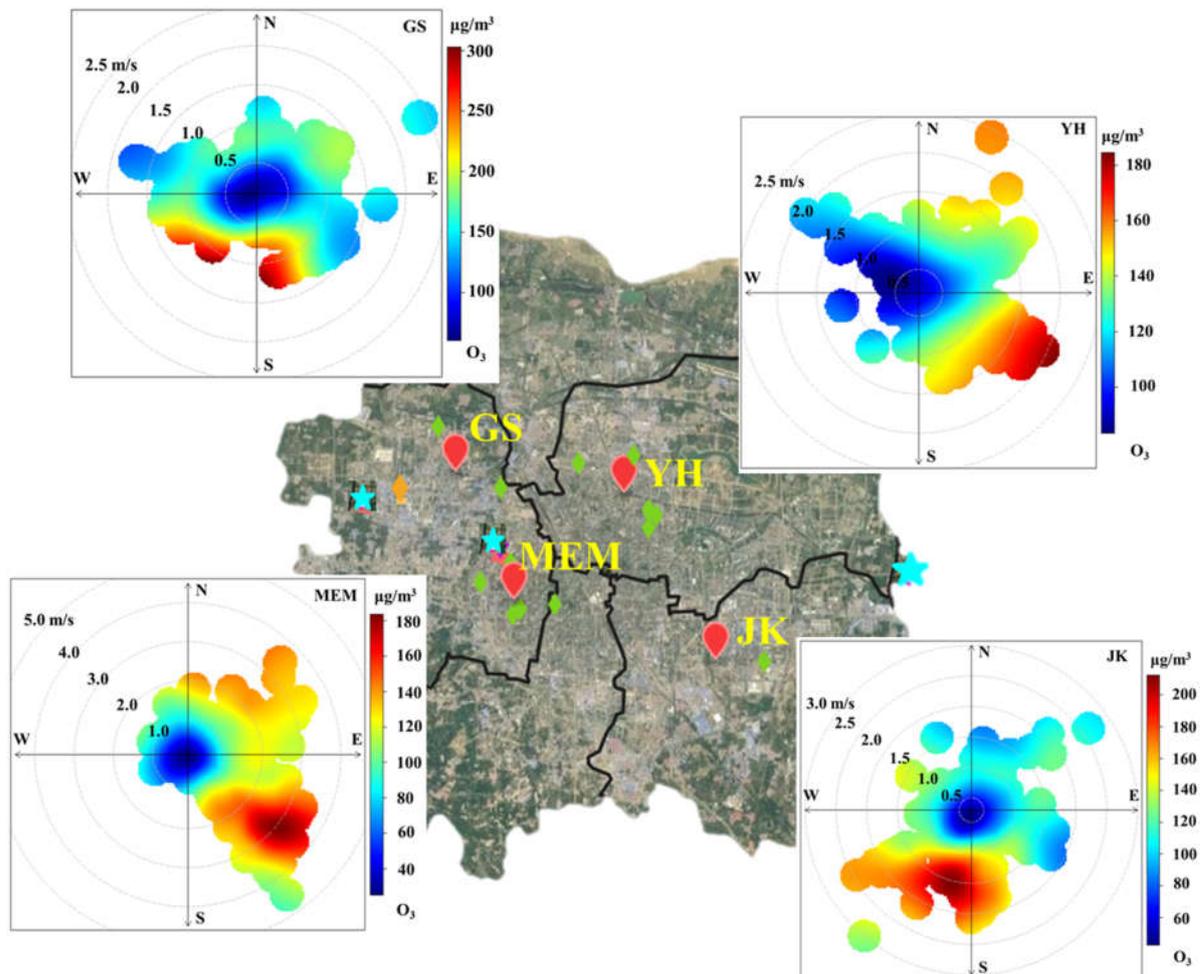
1378 **Response:**

1379

1380 The statement has been revised as

1381

1382 *“The highest total OFP was seen at JK in June, while the highest O<sub>3</sub> levels was*  
1383 *observed at GS where located at a downwind position with lowest WS (0.74±0.33*  
1384 *m s<sup>-1</sup>). The concentration level of O<sub>3</sub> usually increased with wind speed (Fig.S7),*  
1385 *particularly when the eastern wind was dominant, illustrating the disturbance*  
1386 *from long-distance sources to urban center”.*



1387

1388 *Fig.S7 Relationship among O<sub>3</sub> (µg m<sup>-3</sup>), wind direction and wind speed (m s<sup>-1</sup>) during sampling*

1389 *period in June, 2017*

1390

1391 **Source apportionment**

1392

1393 **Comment 45**

1394 It would be extremely useful to have a map showing (roughly) the key emission  
1395 sources for these 7 or 8 factors near each of the 4 sampling sites.

1396

1397 **Response:**

1398

1399 They have been incorporated in newly Fig.1.

1400

1401 **Comment 46**

1402

1403 L420-425: These describe the methodology and should be included in Section 2.

1404

1405 **Response:**

1406

1407 Suggestion taken.

1408

1409 **Comment 47**

1410

1411 L423-424: As suggested previously, I would move Table 6 to SI together with the  
1412 detailed mathematical description of the method

1413

1414 **Response:**

1415

1416 Suggestion taken.

1417

1418 **Comment 48**

1419

1420 L424-425: Explain how the number of factors was determined.

1421

1422 **Response:**

1423

1424 The description has been revised as:

1425

1426 *“Three to nine factors were selected to initiate the running of PMF, the  $Q/Q(\text{exp})$*   
1427 *for every site at fixed factor size were presented in Table S4. With the increase of*  
1428 *factor number, the ratios  $Q/Q(\text{exp})$  were declined due to additional factors. When*  
1429 *the factor size changing from 3 to 4, 4 to 5, and 5 to 6, the decrement of  $Q/Q(\text{exp})$*   
1430 *were larger (~12-23%), while the change was lower than 10% after factors*  
1431 *increased to 7, combined with the field conditions, six factors were defined at*  
1432 *each site.”*

1433

1434 **Comment 49**

1435

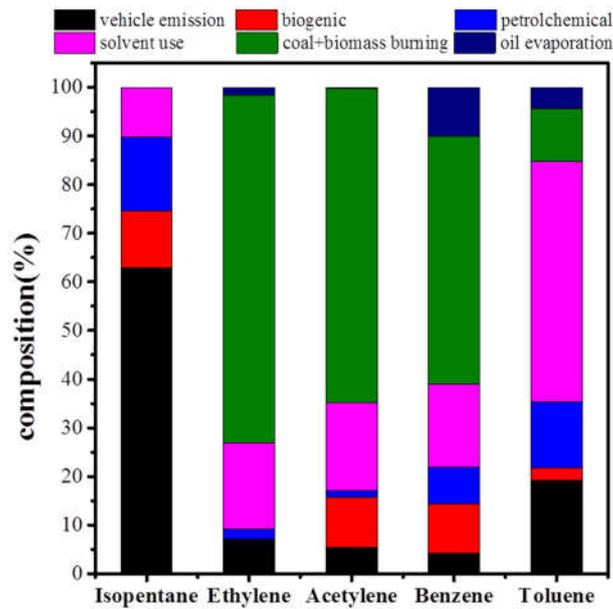
1436 L427-428: Was it possible to identify specific alkanes or alkenes? Were there any clear  
1437 differences between sites or times of day?

1438

1439 **Response:**

1440

1441 Yes, sources can be identified with specific compounds using all of samples collected  
1442 in this study. The PMF results indicate that coal+biomass burning (about 72%) was  
1443 the most important source of ethylene, while as to toluene, solvent use (50%)  
1444 contributed most.



1445

1446

Fig. Major emission sources of abundant compounds apportioned by PMF.

1447

1448 The major emission sources for abundant compounds the four sites were presented  
1449 below:

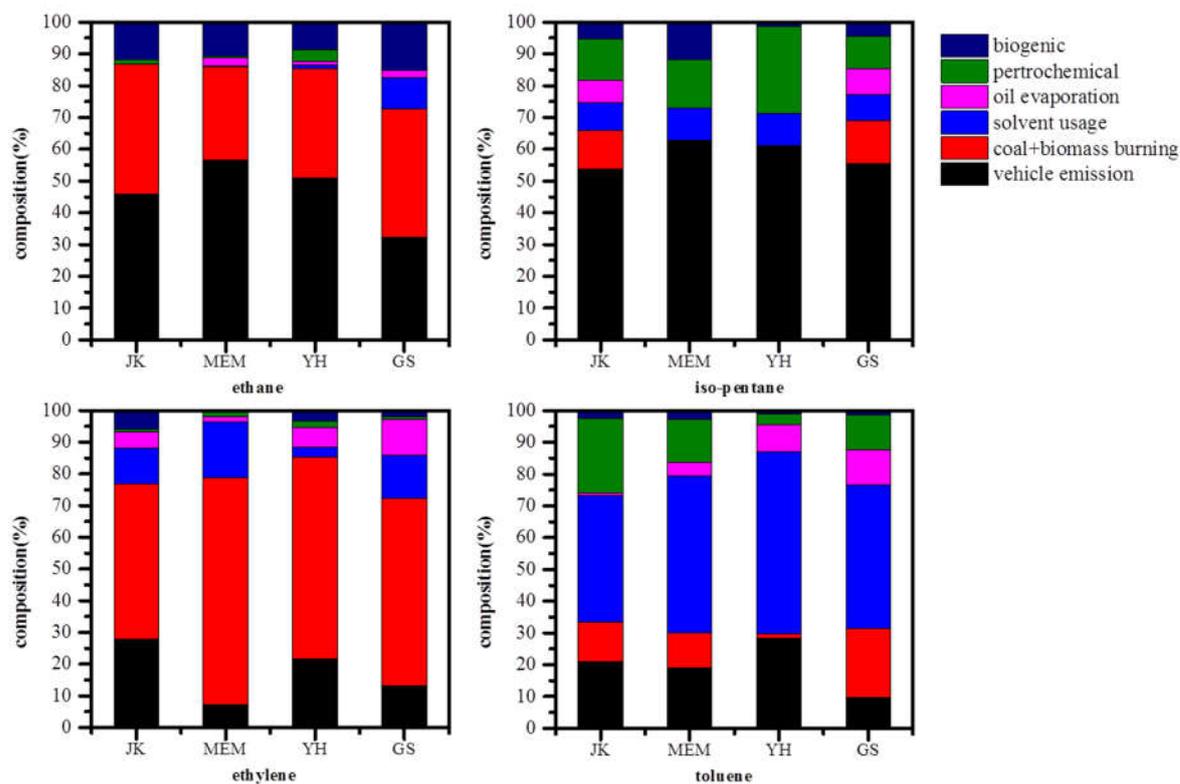


Fig. major sources of ethane, iso-pentane, ethylene and toluene at each site

1450

1451

1452

1453 The major emissions for ethane, iso-pentane and ethylene were combustion-related  
 1454 source. In more specific, vehicle emission and coal+biomass burning were the most  
 1455 important sources for ethane, and vehicle emission contributed more than iso-pentane  
 1456 at each site, while coal and biomass burning contributed most to ethylene regionally.  
 1457 The typical aromatic of toluene is appointed to solvent usage.

1458 **Comment 50**

1459 I suggest the authors emphasize the differences between the identified factors more than they  
 1460 do. It is the trimethylbenzene that distinguishes the second from the first factor, but it is likely  
 1461 that ratios of e.g. toluene to xylene also differ

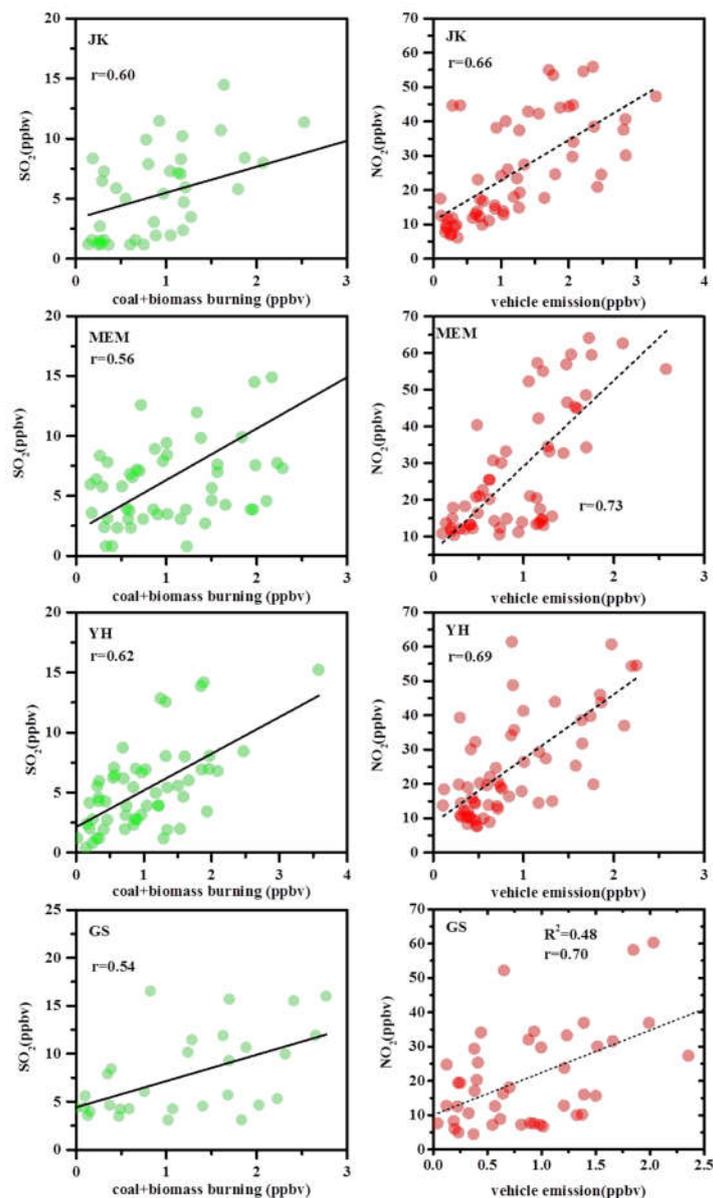
1462 Similarly with source 3: it is the ratio of toluene:benzene and other aromatics that makes this  
 1463 distinct from the first factor and leads to the conclusion that one is gasoline and the other  
 1464 diesel.

1465 Does source 4 also correlate with SO<sub>2</sub> which would strengthen the case that this is specifically  
 1466 coal burning rather than another fossil fuel? Again, the fifth factor seems little different from  
 1467 the first three. Emphasize the unique markers of each

1468

1469 **Response:**

1470 Thanks for the suggestion, we have re-calculated and the correlations are acceptable.



1471

1472 Fig. 16 Correlation analysis between contributions of coal+biomass burning and SO<sub>2</sub>, and vehicle  
 1473 emission and NO<sub>2</sub>

1474 The revised six sources and the correspondent source markers were summarized as below

Source	Source category	Markers	Reference
1	vehicle emission	C <sub>2</sub> -C <sub>5</sub> alkanes, NO <sub>2</sub>	(Watson et al., 2001)
2	coal+biomass burning	ethane, ethylene, acetylene, benzene	(Liu et al., 2008;Zhang et al., 2013)
3	solvent usage	toluene, ethylbenzene, xylenes	(Yuan et al., 2010;Wang et al., 2014)
4	oil gas evaporation	C <sub>4</sub> -C <sub>5</sub> alkenes, n-heptane	(Wang et al., 2017)
5	petrochemical	methyl-cyclopentane, cyclohexane, 3-Methyl-hexane, 2-Methyl-hexane, styrene	(Liu et al., 2008;Jobson et al., 2004)
6	biogenic	Isoprene	(Millet et al., 2016)

1475

1476 **Comment 51**

1477 Source 6 seems to exhibit the same compound mix as source 1. How do they differ? Is it that  
1478 they have very different ratios of some of the compound classes?

1479

1480 **Response:**

1481

1482 We have rerun the PMF, and the problem has been fixed.

1483

1484 **Comment 52**

1485 L465: Do the authors mean different vehicle types (e.g. hybrid, LPG, etc) or different  
1486 styles of driving (e.g. more idling, lower speeds with increased braking, etc)?

1487

1488 **Response:**

1489

1490 It was pointed to different styles of driving.

1491

1492 **Comment 53**

1493 It seems to me that Factor 8 is simply a sub-set of Factor 6. How are they distinguishable?

1494

1495 **Response:**

1496

1497 We have rerun the PMF, and the problem has been fixed.

1498

1499 **Comment 54**

1500 L482-484: It would be really nice if the authors now brought together the two quantified  
1501 analyses they have conducted: source-apportionment and OFPs to identify the sectors  
1502 that were most polluting at each site. Presumably here “important” refers to magnitude  
1503 but would that also be the most important if considering OFP? Or toxicity?

1504

1505 **Response:**

1506

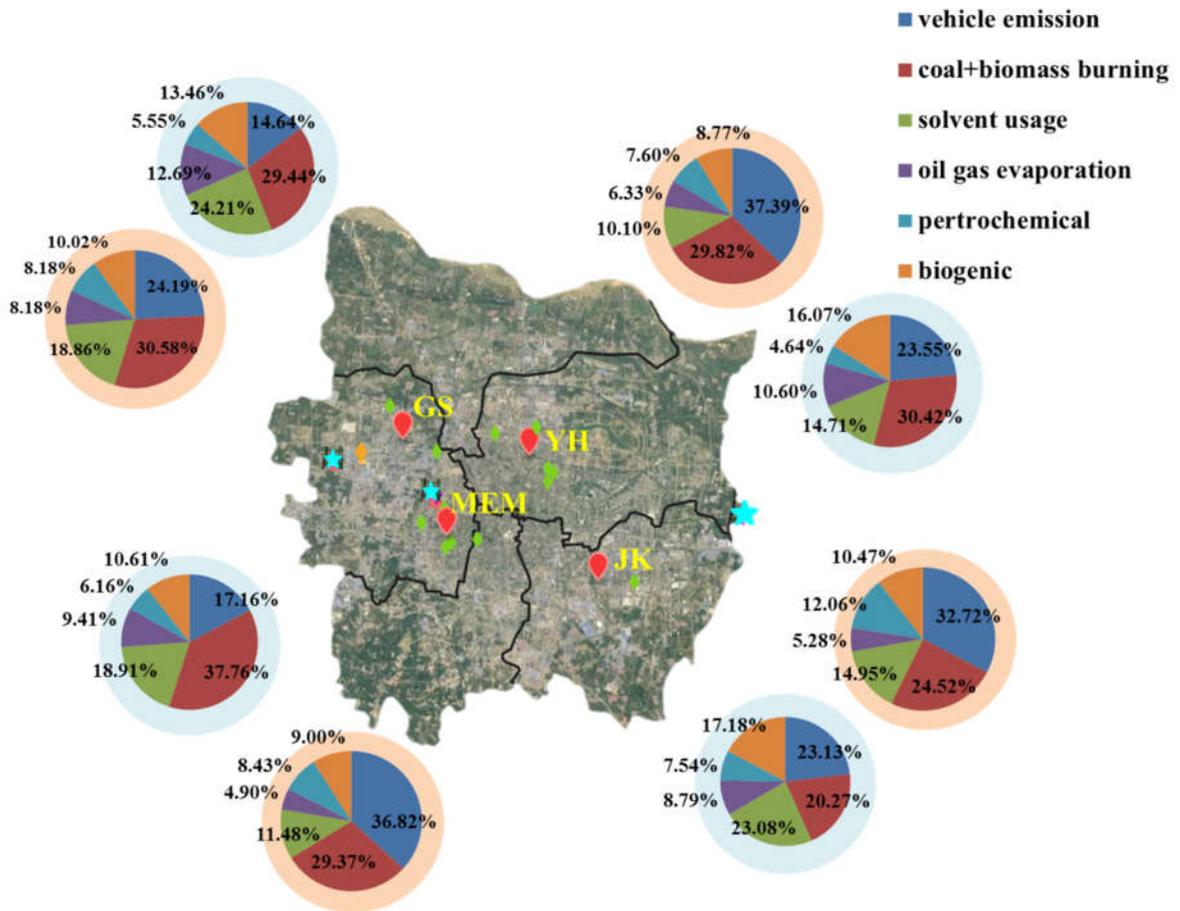
1507 We presented the results on calculation based on two methods, one with absolute  
1508 mixing ratios and the other with OFP, in Fig.17. and a part of description was like  
1509 this:

1510

1511 *“On the base of O<sub>3</sub> formation impact, coal+biomass burning, solvent use, and*  
1512 *vehicle emission were the three major contributors as well. In contrast to the*  
1513 *concentration weighted method, the importance of solvent use estimated with*  
1514 *OFP increased 28-65% for each site, and the significance of vehicle emissions*  
1515 *decreased 29-53%. At YH and GS, small discrimination (<4%) in contributions of*  
1516 *coal+biomass burning between the two methods were found. On the other hand,*  
1517 *the variations on coal+biomass burning at JK (a decline of 17%) and MEM (an*  
1518 *increase of 29%) were more obvious, due to low abundance of reactive species in*  
1519 *this factor at JK and high level of alkenes at MEM. Considering that the aging*

1520  
1521  
1522

*index of xylene/ethylbenzene was high at MEM (2.97) and low at JK (0.01) remarkably, demonstrating that the emission sources related to coal+biomass burning was fresher at MEM than JK.”*



1523  
1524  
1525  
1526

Fig. 17 Source apportionment results during the whole sampling period. The results weighted in observed concentrations were shadowed with pink color, and the results estimated based on OFP were shadowed with light blue color.

1527

**Long-range transport:**

1528

**Comment 55**

1530 This entire section should be moved forward and presented ahead of all the sections  
1531 describing possible local sources of precursor emissions. As O<sub>3</sub> is a secondary  
1532 pollutant, regional and long-range transport is typically the greatest source.

1533

**Response:**

1534

1535 This has been moved to Section 3.1.

1536

**Figures and Tables**

**Comment 56**

1540 Table 1: Suggest move to SI; not essential for main text. However, MIR should be  
1541 included in the current Table 5.

1542 Table 2: See comments regarding wind.

1543 Tables 2-4: Should be combined into a site overview table with all met variables discussed  
1544 within the text, average concentrations of all pollutants, specific VOC concentrations

1545 Table 5: Would suggest to add % contribution to total VOC concentration as a neat  
1546 comparison against % contribution to OFP and to put MIR in this table as it is used to  
1547 calculate OFP

1548 Fig. 1: I suggest the authors combine this with Fig. 10; air mass back trajectories are important  
1549 for virtually all of the analysis presented in this study so should not be relegated to the final  
1550 figure (and similarly should be included far earlier in the text than they are.

1551 Fig. 2: It is not possible for any individual class of VOC to account for >100% of the  
1552 composition of total VOCs. Either the authors should be using a stacked bar chart with each  
1553 segment of the bar representing the different compound classes or a side-by-side bar chart as  
1554 in the insert for isoprene. I would also suggest that isoprene should be included as part of the  
1555 chart and not as an insert.

1556 There is no obvious reason why the right-hand and left-hand panels should use different types  
1557 of chart given they are showing the same thing.

1558 The caption should be expanded to actually explain the figure; it is not just a title. For  
1559 example, do the bars for YH, GS, etc on the left-hand panel include both 07:00 and 14:00 data?  
1560 And is that comparable with the data from other cities? The panel would be less cluttered if  
1561 the authors listed the references as footnotes rather than on the chart itself.

1562 Fig. 3: This figure is very poorly presented. The authors are attempting to fit too much data on  
1563 each panel with too few different axes scales. Using a reverse scale on the secondary y-axis  
1564 makes it almost impossible to assimilate the information and see correlations between the  
1565 different variables. Using an axis ranging from 0 to 200 means that the T (in degC) is  
1566 compressed to the point of masking any hour-to-hour fluctuations; CO (even scaled to ppm  
1567 instead of ppb) has become a featureless red  
1568 line. Why is SO<sub>2</sub> coloured in rather than just presented as a line?

1569 The data requires splitting across additional panels, firstly helping to de-clutter and secondly  
1570 allowing additional axes for clarity.

1571 Again the caption should be expanded to be more descriptive. What is the significance of the  
1572 two dates that are shaded? Are the tick marks corresponding to the dates shown at the bottom  
1573 indicating 00:00 on that date? Or 12:00 (i.e. the middle of the day)?

1574 Fig. 4: Why are the colours used for each class here (and in Fig. 3) different from those used  
1575 in the left-hand panel of Fig. 2 ?

1576 Given that the left-hand panel has a continuous temporal scale on the x-axis would it make  
1577 more sense to present all 07:00 data before all 14:00 data on right-hand panel rather than  
1578 splitting by site?

1579 Please include more information in the figure caption.

1580 Fig. 5: Again, the authors are attempting to fit too many different variables on each panel,  
1581 each with different scales, chart types, symbols and symbol colours. This requires splitting out  
1582 into separate panels or charts.

1583 **Response:**

1584

1585 [Tables and figures have been revised according to the suggestion.](#)

1586 **Change list**

1587 **Title**

1588 Changed as “Characterization of VOCs and their related atmospheric processes in a  
1589 central China city during severe ozone pollution periods”

1590

1591 **Abstract**

1592 **L17-19** “Canister samples were collected for measurement of fifty-seven VOCs,  
1593 which are the most important O<sub>3</sub> precursors.”

1594 **L23-27** “The cluster analysis points out that air masses from cities south of  
1595 Zhengzhou were cleaner than from other directions. Besides, the molar ratio of VOCs  
1596 to NO<sub>x</sub> indicated that VOCs were more sensitive than NO<sub>x</sub> to the O<sub>3</sub> formation in  
1597 Zhengzhou. Meanwhile, the overall results further implied that photochemical  
1598 reactions at marginal sites where highly distributed with industries were more  
1599 efficient than those at other sites.”

1600 **L30-34** “From Potential Source Contribution Function (PSCF) analysis, the strong  
1601 emissions from coal+biomass burning and solvent usage were concentrated in  
1602 southwest of Shanxi and Henan province. The results of this study gather scientific  
1603 evidences on the pollution sources for Zhengzhou city, benefiting the Government to  
1604 establish efficient environmental control measures particularly for O<sub>3</sub> pollution.”

1605

1606 **1. Introduction**

1607 **L42-49** “In China, the investigations on VOCs including source apportionment,  
1608 measurement of emission profiles and interpretation of seasonal variations were  
1609 mainly concentrated in Yangtze River Delta (YRD), Pearl River Delta (PRD) and  
1610 Beijing-Tianjin (BJT) regions (An et al., 2014;Wang et al., 2014;Chen et al., 2014;Liu  
1611 et al., 2016;Guo et al., 2017). Limited studies have been conducted in less developed  
1612 or developing regions (i.e., southwestern and northwestern China) where prominently  
1613 impacted by biomass burning and with high abundances of toxic and reactive  
1614 compounds (Li et al., 2014;Li et al., 2017a).”

1615 **L50-65** “Fifty-seven VOCs, including C<sub>2</sub> - C<sub>10</sub> alkanes, alkenes, alkynes and  
1616 aromatics, which greatly contribute to ambient O<sub>3</sub> formation, have been identified and  
1617 are regularly monitored by Photochemical Assessment Monitoring Stations (PAMS)  
1618 (Shao et al., 2016;Chen et al., 2010). Due to characteristic structure and reactivity of  
1619 these compounds, their contributions in O<sub>3</sub> production were varied accordingly, and it  
1620 is reported that aromatics and alkenes were responsible for most of the weighted  
1621 reactivity of VOCs (59.4% and 25.8%, respectively) in Pearl River Delta (PRD)  
1622 region in China (Ou et al., 2015). Consequently, researchers have deduced that  
1623 reductions of alkenes and aromatics are profit for O<sub>3</sub> control (Carter, 1994). In  
1624 addition, with the variations on energy structure, industrial construction and  
1625 meteorological conditions (Wang et al., 2015;Shao et al., 2011), major emission  
1626 sources of VOCs at each city are unique. In less developed cities of Heilongjiang and  
1627 Anhui, biomass combustion had the highest contribution (40% and 36%, respectively)  
1628 to the O<sub>3</sub> formation potentials due to high quantity of agricultural activities, while in

1629 the developed cities such as Shanghai, Beijing and Zhejiang, solvent usage has  
1630 become more dominant (>20%) than other pollution sources (Wu and Xie, 2017).  
1631 Therefore, identification on district emission sources of VOCs is necessary to provide  
1632 scientific-based information for policy-makers who establish efficient strategies to  
1633 alleviate O<sub>3</sub> pollution.”

1634 **L66-74** “In addition to the factors discussed above, non-linear relationships between  
1635 ambient VOCs, nitrogen oxide (NO<sub>x</sub>) and O<sub>3</sub> production indicate that the reduction in  
1636 tropospheric O<sub>3</sub> is more complex than expected (Lin et al., 1998;Hidy and Blanchard,  
1637 2015;Li et al., 2018). Many modeling and field studies showed that photochemical O<sub>3</sub>  
1638 production in several cities in China such as Guangzhou, Shanghai and Beijing with  
1639 high levels of NO<sub>x</sub> were highly sensitive to VOCs (Shao et al., 2009;Gao et al.,  
1640 2017;Ou et al., 2016). The sensitivity regime is always varied with time and  
1641 geographical locations (Luecken et al., 2018). The percentage of VOC-limited regime  
1642 in North China Plain (NCP) increased from 4% to 6% between 2005-2013, owing to  
1643 the rapid increases of NO<sub>x</sub> emissions (Jin and Holloway, 2015).”

1644 **L79-82** “The Air quality index (AQI) for 65% of the days in 2013 exceeded the  
1645 allowable limits of 100 established by the Air Quality Guideline. Particularly, O<sub>3</sub> was  
1646 the major pollutant in summer and over 50% of the days in a year, the mixing ratio of  
1647 O<sub>3</sub> exceeded the Grade I standard (100 μg m<sup>-3</sup>) of daily maximum average 8-hour  
1648 (DMA8) in Henan (Shen et al., 2017;Gong et al., 2017).”

1649

## 1650 **2. Observation and Methodology**

### 1651 **2.1 Sampling site**

1652 **L93-94** “Based on the density of population distribution, locations of industrial  
1653 facilities, and the prevailing winds, four sites have been selected for sample  
1654 collection:”

1655 **L106-111** “Ten sampling days with the rainfall record (*ca.* 0 mm) were chosen in  
1656 every month during the period of May - September, 2017 consequently, to represent a  
1657 typical air quality condition in a month. Grab samples were collected minute using 3.2  
1658 L stainless-steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA), which  
1659 were pre-cleaned with high purity nitrogen and pressurized to 20 psi. Two samples,  
1660 one collected at 07:00 with increasing of human activities and another one collected at  
1661 14:00 with well-mixed of ambient air, were obtained on each sampling day.”

1662

### 1663 **2.2 Chemical Analysis**

1664 **L128-131** “Target compounds were identified with retention time and mass spectra,  
1665 and quantified with multi-point calibration curve in this study. The standard gas of  
1666 PAMS (1 ppm; Spectra Gases Inc, NJ, USA) was used to construct the calibration  
1667 curves for the 57 target VOCs, including 28 alkanes, 11 alkenes, acetylene and 17  
1668 aromatics.”

1669 **L137-140** “Due to the complex chemical reactions, the application of PMF in VOCs  
1670 has to be based on a couple of principles: eliminating species with mixing ratios  
1671 below MDL and excluding species with high reactivity, except for the source markers

1672 (Shao et al., 2016;Guo et al., 2011). Finally, 31 VOC species and NO<sub>2</sub> were chosen for  
1673 the source apportionment analysis.”  
1674

### 1675 **2.3 Positive matrix factorization (PMF)**

1676 **L141-155** “In this study, PMF was performed with fifty base runs for each site, results  
1677 with the minimum Q value (a parameter used to express uncertainties of PMF results)  
1678 were considered as optimum solutions. In Table S2 the r<sup>2</sup> between observed values  
1679 and predicted values of selected VOCs and NO<sub>2</sub> are presented for the four sites, the r<sup>2</sup>  
1680 for most species (>80%) were higher than 0.6, compounds with r<sup>2</sup><0.6 were down  
1681 weighted when determine factor sources.

1682 During PMF analysis, bootstrap method was used to evaluate stability and  
1683 uncertainty of the base run solution, setting the minimum correlation R-value at 0.6,  
1684 100 bootstrap runs were performed, and the results were showing in Table S3, and  
1685 acceptable results (>80%) were gained for all the factors.

1686 Three to nine factors were selected to initiate the running of PMF, the Q/Q(exp)  
1687 for every site at fixed factor size were presented in Table S4. With the increase of  
1688 factor number, the ratios Q/Q(exp) were declined due to additional factors. When the  
1689 factor size changing from 3 to 4, 4 to 5, and 5 to 6, the decrement of Q/Q(exp) were  
1690 larger (~18-25%), while the change was lower than 12% after factors increased to 7,  
1691 combined with the field conditions, six factors were defined at each site.”  
1692

### 1693 **2.4 Potential source contribution function (PSCF)**

1694 This was a newly section  
1695

### 1696 **2.5 Estimation of the initial NO<sub>x</sub> and VOCs**

1697 This was a newly section  
1698

## 1699 **3 Results and discussions**

### 1700 **3.1 Meteorological variations and Mixing ratios**

1701 **L188-200** “Meteorological conditions are important factors that impact both the  
1702 compositions and levels of VOCs. During the sampling period, the T (RH) was varied  
1703 from 15°C (15%) to 38°C (100%) (Fig.S1), and the dominant wind was northwestern  
1704 and southeastern (Fig. 2). The air clusters, analyzed by HYSPLIT model, showed  
1705 moderate differences in each month (Fig. 3). In May, clusters arriving at Zhengzhou  
1706 demonstrated longer paths, and included six clusters in total, while in June, the length  
1707 of clusters were shorter. However, the concentration levels and compositions of VOCs  
1708 were similar in the two months. In May, the largest cluster (27.2%) was passed over  
1709 from Yinchuan, a central city in northwest China, then crossing several non-capital  
1710 cities (i.e., Yanan, Yuncheng and Luoyang) in Shanxi and Sichuan provinces. Such a  
1711 long-range transport of pollutants might result a less impact on the air quality of  
1712 Zhengzhou, as comparable level and similar compositions of VOCs were obtained  
1713 during the period of May - June. In June, August and September, approximately half  
1714 of the air trajectories originated from the areas of Henan province, indicating the air  
1715 pollutants in Zhengzhou were impacted by local factors at most time.”

1716 **L201-203** “The  $\Sigma_{\text{VOCs}}$  varied at the four sites, where the highest  $\Sigma_{\text{VOCs}}$  and their  
1717 compositions were not identical across the sampling months as well.”

1718 **L207-209** “This can be attributed to numerous factors that will be explored later in the  
1719 paper. Besides the emission sources (to be discussed in Section 3.2), the impacts  
1720 controlled by meteorological conditions should not be ignored as well.”

1721 **L214-216** “The air pollutants emitted from MEM and YH were more liable resulting  
1722 in a higher level of  $\Sigma_{\text{VOCs}}$  at GS in June.”

1723 **L219** “where the elevation was gradually increased from east to west in Zhengzhou  
1724 (Mu et al., 2016).”

1725 **L227** “which was mainly emitted from biogenic sources and increased exponentially  
1726 with ambient temperature (Jiang et al., 2018).”

1727 **L235-237** “the composition of alkanes was the largest in all cities because of their  
1728 longer lifetimes and widespread from a variety of pollution sources (Fig. 5), while the  
1729 composition of aromatics was lower than alkenes in these cities except for  
1730 Guangzhou.”

1731 **L241-242** “the composition of aromatics in Zhengzhou was the lowest probably due  
1732 to its less solvent-used manufacturers than in Guangzhou, Hangzhou and Nanjing, and  
1733 less numbers of vehicles than in Beijing.”

1734 **L245-246** “Zhu et al. (2016) observed that the composition of alkyne in the  
1735 biomass-burning period could be double of that in the non-biomass burning period.”

1736

### 1737 **3.2 Temporal variations**

1738 **L257-258** “The occurrences of precipitation and raining were also frequent in most  
1739 areas of China during summer, resulting in decreasing background level of air  
1740 pollutants.”

1741 **L267-274** “Beside local emissions, the long-range air mass also had some impacts on  
1742 relatively lower level of  $\Sigma_{\text{VOCs}}$  in July. As illustrated in Fig.3, different from other  
1743 months, the air current was originated with the largest portion (*ca.* 88.68%) of clusters  
1744 from Hubei province, where the average  $\Sigma_{\text{VOCs}}$  in its capital city ( $23.3 \pm 0.6$  ppbv) (Lyu  
1745 et al., 2016) was lower than that in Zhengzhou ( $29.18 \pm 23.08$  ppbv). In combination  
1746 with the lower weight percentage of photothermal-reactive aromatics ( $10.30 \pm 4.23\%$ ),  
1747 and the lowest toluene to benzene (T/B) ratio of  $1.15 \pm 0.99$  around this period, it is  
1748 possible that the cleaner air mass clusters originating from Hubei also contributed to  
1749 the reduction of  $\Sigma_{\text{VOCs}}$  in July.”

1750 **L281-285** “Specifically, at MEM, the distinctive increment was always accompanied  
1751 with obvious increases of alkanes or aromatics (Fig. 7). Since the T and RH were  
1752 often consistent during the sampling period, the direct gas evaporations should be  
1753 constant as well. Therefore, the simultaneous increased concentrations of  $\text{SO}_2$ , CO  
1754 and  $\text{NO}_x$  could illustrate the potential impacts from combustion sources, such as  
1755 emissions from nearby thermal power plant.”

1756

### 1757 **3.3 Spatial variations**

1758 **L299-308** “The  $\text{C}_2$  -  $\text{C}_5$  alkanes, acetylene, ethylene, toluene and benzene were the  
1759 most abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene

1760 varied within a wide range at each site, because of its universal emission sources (e.g.,  
1761 vehicle exhaust emissions and solvent usage) (Wang et al., 2014; Barletta et al., 2005).  
1762 These chemicals contributed >60% for  $\Sigma_{\text{VOCs}}$  at each site, illustrating strong  
1763 combustion-related sources in Zhengzhou.

1764 Among the four major organic classes, alkane was the most abundant group as a  
1765 result of its widespread sources and longevity (Fig.5), accounted for 52.9%, 62.5%,  
1766 53.4%, 53.4% of the total  $\Sigma_{\text{VOCs}}$  at JK, MEM, GS, and YH, respectively. The highest  
1767 composition of alkane was observed at MEM due to the stronger contributions of  
1768 ethane, iso-pentane, and C<sub>6</sub>-C<sub>8</sub> branched alkanes (Fig. S3), which are emitted from  
1769 light-duty gasoline vehicles (Wang et al., 2017a).”

1770 **L312-315** “Under high levels of VOCs and sufficient supply of NO<sub>x</sub>, the highest  
1771 average mixing ratio of O<sub>3</sub> was observed at GS, followed by YH where even with the  
1772 lowest VOCs and NO<sub>x</sub>, indicating that there are multiple factors, rather than the  
1773 absolute concentrations, contributed to the O<sub>3</sub> formation at YH.”

1774 **L320-325** “The higher level of O<sub>3</sub> at GS was accompanied with the higher  $\Sigma_{\text{VOCs}}$   
1775 ( $39.29 \pm 25.37$  ppbv). The weight percentage of aromatics ( $15.62 \pm 12.06\%$ ) at GS was  
1776 higher than those at other sites as well, indicating that the painting and other  
1777 renovation activities at GS was potentially an important factor for its high O<sub>3</sub> level in  
1778 June. Even though both the  $\Sigma_{\text{VOCs}}$  and specifically high O<sub>3</sub> formation potential  
1779 compounds (such as alkenes and aromatics) at MEM were slightly higher than those  
1780 at YH (Table 4), the O<sub>3</sub> concentration at MEM was not higher.”

1781 **L330-334** “For example, Streets et al. (2007) reported that with continuous southern  
1782 winds, the O<sub>3</sub> level in Beijing was 20-30% contributed from its neighboring cities in  
1783 Hebei. During this study, a typical regional ozone pollution was happened on August  
1784 10<sup>th</sup> at YH (Fig.6). On that day, the ratios of  $\Sigma_{\text{VOCs}}/\text{NO}_x$  at the four sites were all less  
1785 than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional VOC-control system, and that  
1786 VOCs are the critical contributors to the formation of O<sub>3</sub> in Zhengzhou.”

1787 **L339-340** “All of this confirmed that the abnormally high O<sub>3</sub> at YH was caused by the  
1788 transport of air pollutants from other sites on that day.”

1789

### 1790 3.4 VOCs/NO<sub>x</sub> ratio

1791 This was a newly added section

1792

### 1793 3.5 Ratios of specific compounds

1794 **L374-380** “The ratio of i-pentane to n-pentane can be used to differentiate potential  
1795 sources such as consumption of natural gas, vehicle emissions and fuel evaporations.  
1796 It is claimed that in areas heavily impacted by natural gas drilling, the ratios were lied  
1797 within the range of 0.82 - 0.89 (Gilman et al., 2013; Abeleira et al., 2017). Higher  
1798 values were often reported for automobiles, in a range of 2.2 - 3.8 for vehicle  
1799 emissions, 1.8 - 4.6 for fuel evaporation, and 1.5 - 3.0 for gasoline (Russo et al.,  
1800 2010; McGaughey et al., 2004; Jobson et al., 2004; Wang et al., 2013), whereas the  
1801 ratios below unity was found for coal combustion (0.56 - 0.80) (Yan et al., 2017).”

1802 **L385-387** “The average ratio at MEM was 2.31, higher than the character ratios of  
1803 coal combustion, reasonably due to the observation site presented at upwind position

1804 of the thermal power plant.”

1805 **L390-391** “The average ratios at YH (1.94) and GS (1.63) were lower than those at  
1806 the above two sites, suggesting the comparatively stronger contribution from coal  
1807 burning.”

1808 **L398-419** “In this study, the correlation between benzene and toluene was fairly well  
1809 at all the sites ( $R^2=0.70-0.74$ ), except for YH ( $R^2=0.41$ ) (Fig.14), suggesting the  
1810 similar sources for benzene and toluene at JK, MEM and GS, while more complex  
1811 such as variable wind direction at YH. The average ratios of T/B were lied within the  
1812 range of 1.64-2.29, which were scattered around the character ratio of 2 for vehicle  
1813 exhaust, illustrating the significance of vehicle emissions at the four sites. Specifically,  
1814 at JK, MEM and YH, most of T/B ratios were distributed between 0.6 and 3, which  
1815 were corresponding to character ratios for coal or biomass burning and industrial  
1816 activities respectively. These reflected the mixture impacts from mobile source and  
1817 coal/biomass burning at these three sites. However, more values were greater than 3 at  
1818 GS, suggesting more frequent disturbance from industrial activities at this site.

1819 From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00  
1820 LT (Fig.15). In fact, the reaction rate constant of toluene ( $5.63 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )  
1821 with  $\bullet\text{OH}$  is much higher than that for benzene ( $1.22 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ),  
1822 representing more rapid consumption of toluene from photochemical reactions and  
1823 thus resulting in lower T/B ratios at 14:00 LT. Besides, the emission strength of  
1824 mobile source is often weaker at 14:00 LT, while the coal/biomass burning are  
1825 increased due to more human activities. Both of the situations can be used to explain  
1826 the lower T/B ratios observed at 14:00 LT. In comparison with other months, higher  
1827 T/B ratios were found more frequently in September, potentially showing the more  
1828 strengthen industrial activities during this period.

1829 Overall, based on the iso-pentane/i-pentane and T/B ratios, the atmospheric  
1830 VOCs at every site were impacted by a mix of coal/biomass burning and vehicle  
1831 emissions, whereas GS was more liable impacted by industry-related sources.”

1832

### 1833 **3.6 Relative reactivity of VOCs**

1834 **L421-426** “The reactivity of individual species was different, while mixtures of VOCs  
1835 would have competition the precursors between each other, leading to variations on  
1836 reaction paths and  $\text{O}_3$  formation yields. Ozone formation potential (OFP) is a useful  
1837 tool to estimate maximum  $\text{O}_3$  productions of each compound under optimum  
1838 conditions, from which the vital species in  $\text{O}_3$  formation could be identified (Huang et  
1839 al., 2017). The calculation of OFP is based on mixing ratios and maximum  
1840 incremental reactivity (MIR) of individual compound,”

1841 **L431-435** “In Zhengzhou city, alkenes contribute most ( $55.91 \pm 14.17\%$ ) to the sum  
1842 of OFP, of which ethylene had the largest portion. The results is different with the  
1843 estimation based on emission inventories by Wu and Xie (2017), in which the largest  
1844 contributor of total OFP in North China Plain (NCP), YRD and PRD was aromatics,  
1845 reflecting that there was relatively less surface coating industries in Zhengzhou.”

1846 **L449-456** “Under low RHs and high T and OFP ( $88.13 \pm 30.32$  ppbv), the  $\text{O}_3$  level at  
1847 YH was unexpectedly lower than that at MEM on sunny days. Since the OFP was

1848 estimated with the assumption of reactions that proceeded under optimum conditions,  
 1849 the above phenomenon reflected there were unsatisfied O<sub>3</sub> formation conditions at YH.  
 1850 The highest total OFP was seen at JK in June, while the highest O<sub>3</sub> levels was  
 1851 observed at GS where located at a downwind position with lowest WS (0.74±0.33 m  
 1852 s<sup>-1</sup>). The concentration level of O<sub>3</sub> usually increased with wind speed (Fig.S7),  
 1853 particularly when the eastern wind was dominant, illustrating the disturbance from  
 1854 long-distance sources to urban center.”

1855

### 1856 **3.7 Source apportionment**

1857 This whole section has been rewritten

1858

### 1859 **3.8 Consumption of VOCs and correlations with ozone level**

1860 This was a newly added section

## 1861 **4. Conclusions**

1862 **L522-523** “It is found that the weighted percentage of aromatics was lower, while  
 1863 alkyne was higher in Zhengzhou city than in other Chinese cities.”

1864 **L529-540** “In addition, the impact of aging process was less in Zhengzhou than that  
 1865 in Beijing. The photochemical reactions at JK and GS were more efficient, while the  
 1866 relationships among O<sub>3</sub>, NO<sub>x</sub> and VOCs at urban sites of MEM and YH were more  
 1867 complex. Either the mixing ratios or calculated OFPs demonstrated that the most  
 1868 important contributors to VOCs were vehicle exhaust, coal+biomass burning and  
 1869 solvent use, illustrating the necessary to conduct emission controls on these pollution  
 1870 sources. Vehicle emission was more dominant at urban center (YH and MEM), while  
 1871 solvent use was more important at the sites (JK and GS) far away from urban center in  
 1872 Zhengzhou. It is further shown that the air pollution in Zhengzhou was mostly  
 1873 impacted by local emissions according to the cluster analysis, and southern air  
 1874 clusters occasionally from Hubei Province was cleaner. In addition, strong emissions  
 1875 for coal+biomass burning were concentrated in southwest of Shanxi, western of  
 1876 Shandong and southwest of Henan provinces according to the PSCF analysis.”

1877

### 1878 **Table & Figure**

1879 All of the tables and figures were reconstructed thoroughly.

1880

1881 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

1882

1883

1884

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

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

1885

1886 Table3. Concentration levels of VOCs and compositions of major groups in Zhengzhou and other  
1887 cities in China

Items	Guangzhou	Nanjing	Beijing	Hangzhou	Wuhan	Zhengzhou
	March-December, 2005	2011-2012	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
Compositions of major groups (%)	<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., 2017b)	(Lyu et al., 2016)	this study

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1889 Table4. Specific information on VOCs, O<sub>3</sub> 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
$\Sigma_{\text{VOCs}}$ (ppbv)	34.02	30.28	28.33	39.29
O <sub>3</sub> (ppbv)	74.87	73.50	73.81	87.99
NO(ppbv)	7.10	7.72	2.34	4.47

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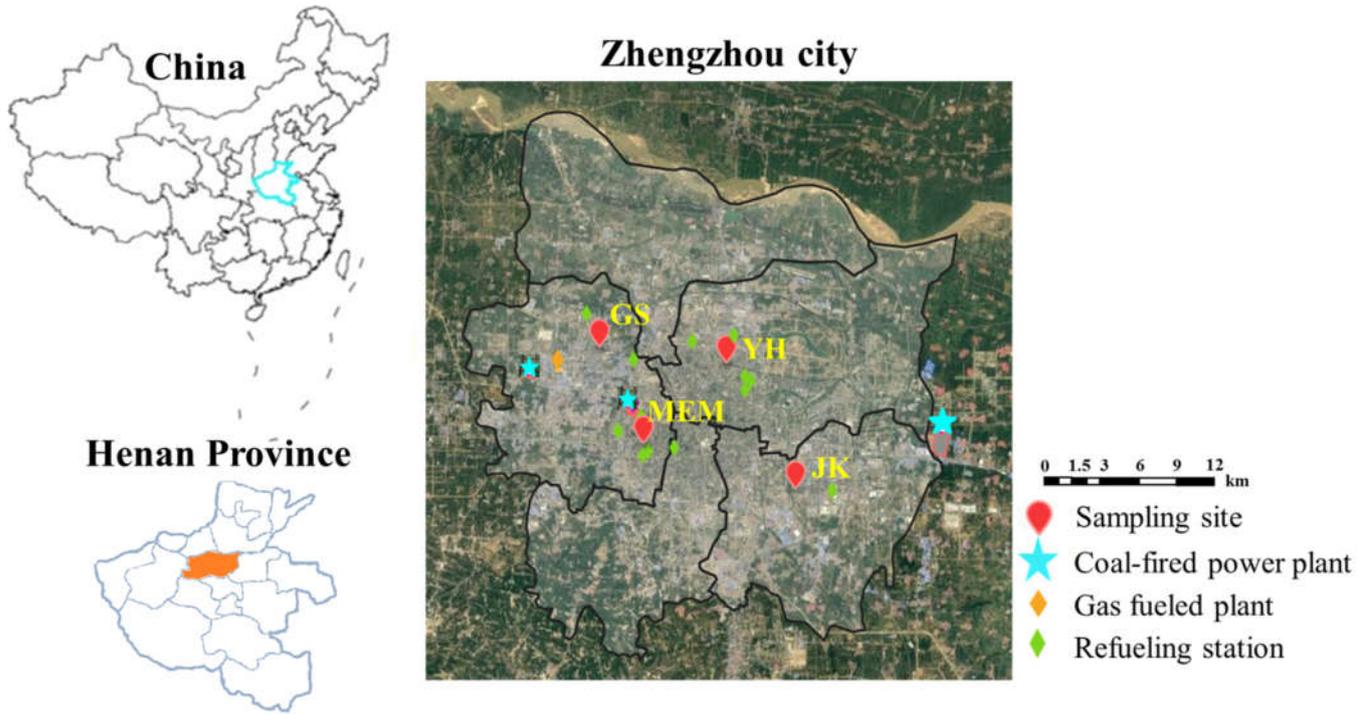
1899 Table5. Top 10 VOCs ranked according to calculated ozone formation potential (OFP) and their  
 1900 corresponding percentage weighted in mixing ratio

Site	Species	OFP (ppbv)	Weighted in OFP (%)	Weighted in mixing ratio (%)	Site	Species	OFP (ppbv)	Weighted in OFP (%)	Weighted in mixing ratio (%)
JK	Ethylene	18.99	25.54	8.22	MEM	Ethylene	18.44	30.88	7.92
	Isoprene	12.99	21.83	7.31		Isoprene	4.66	10.10	2.36
	m/p-Xylene	6.08	5.89	2.67		Toluene	3.73	6.67	3.99
	Toluene	5.53	5.83	4.22		Propylene	3.60	6.16	1.25
	Propylene	4.03	5.36	1.29		Acetylene	2.82	5.00	12.19
	Acetylene	2.97	4.44	13.54		m/p-Xylene	2.55	4.20	1.40
	n-Butane	2.15	3.05	7.28		n-Butane	1.81	3.20	5.97
	o-Xylene	1.83	2.00	0.88		Isopentane	1.76	3.16	7.39
	Isopentane	1.66	1.95	6.50		Ethane	1.58	2.96	23.35
	Propane	1.17	1.73	9.77		Propane	1.31	2.48	10.64
YH	Ethylene	19.83	28.10	8.88	GS	Ethylene	18.04	25.96	7.51
	Isoprene	7.44	11.30	3.67		Isoprene	8.01	16.75	4.64
	Toluene	6.63	7.75	5.72		Toluene	7.43	7.67	5.49
	m/p-Xylene	3.93	4.38	1.58		Propylene	4.39	5.85	1.26
	Acetylene	3.15	4.38	13.91		m/p-Xylene	4.31	4.57	1.75
	Propylene	3.01	3.60	0.91		Acetylene	2.76	4.24	12.07
	Trans-2-pentene	2.25	2.94	3.43		n-Butane	1.82	2.93	6.39
	n-Butane	1.84	2.80	6.31		Isopentane	1.71	2.68	6.94
	Isopentane	1.59	2.22	6.69		Propane	1.38	2.26	11.61
	Propane	1.18	1.98	10.20		Isobutane	1.13	1.98	4.59

1901 <sup>a</sup> *m*-Xylene and *p*-Xylene are co-eluted in the chromatographic separation.

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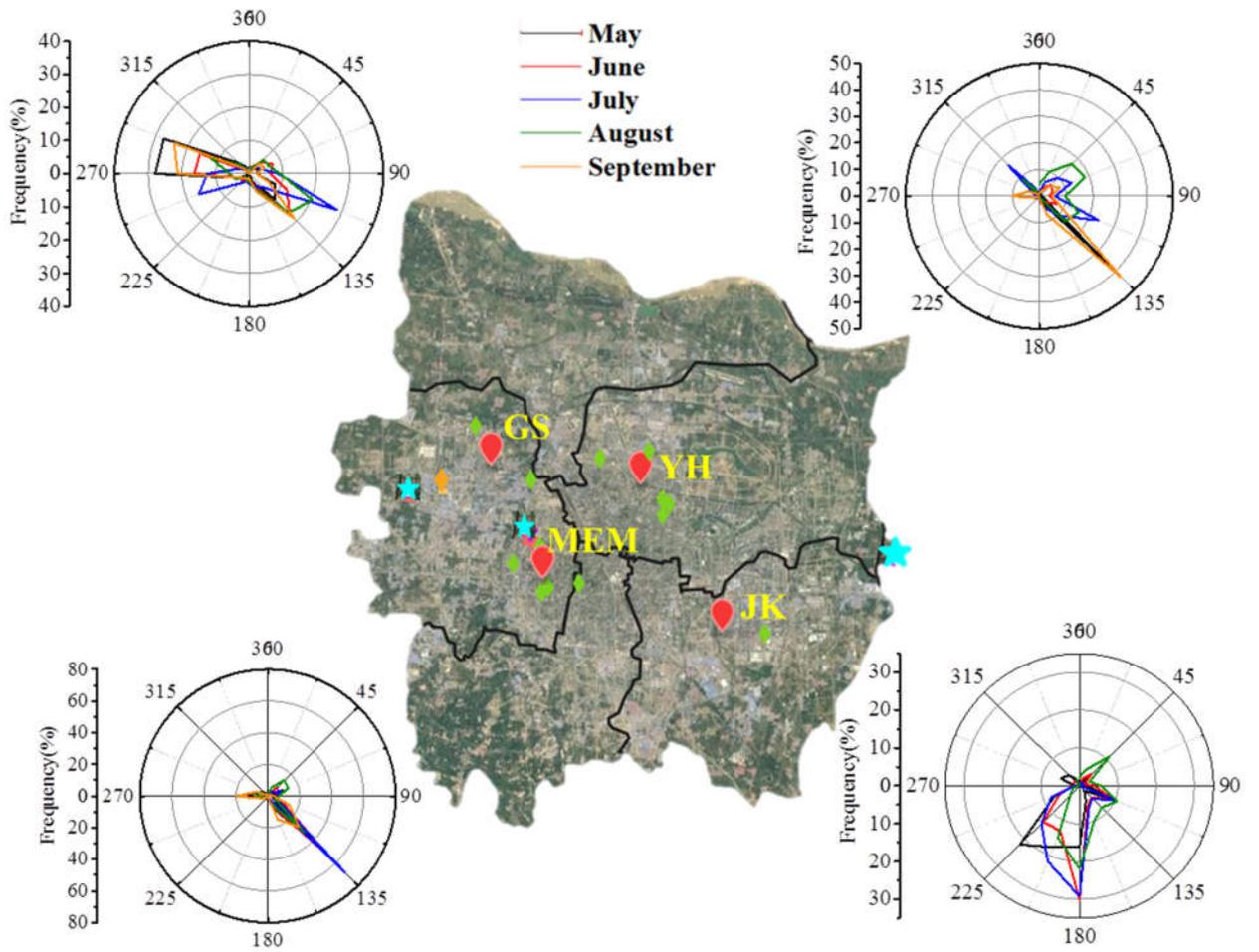


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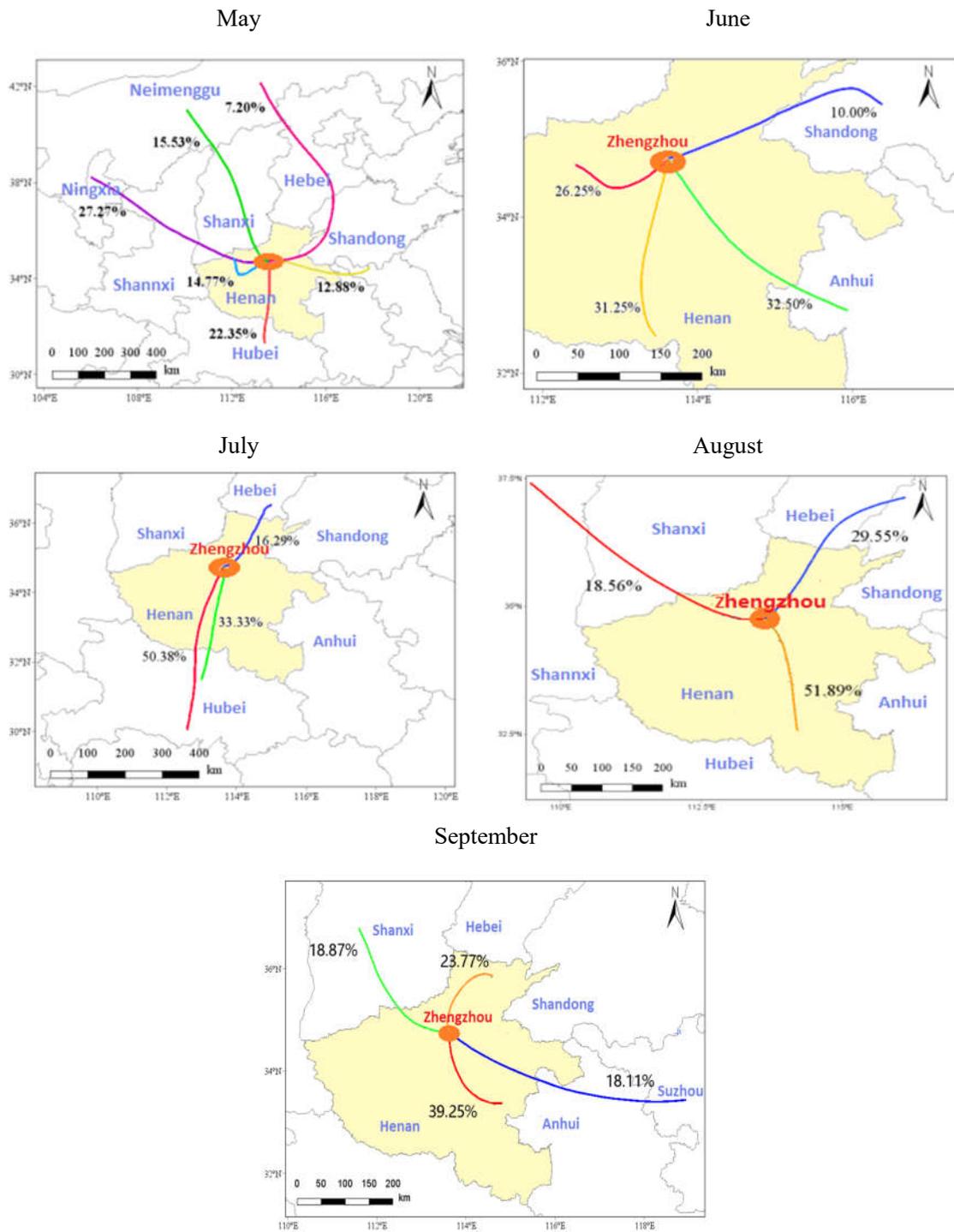
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Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.



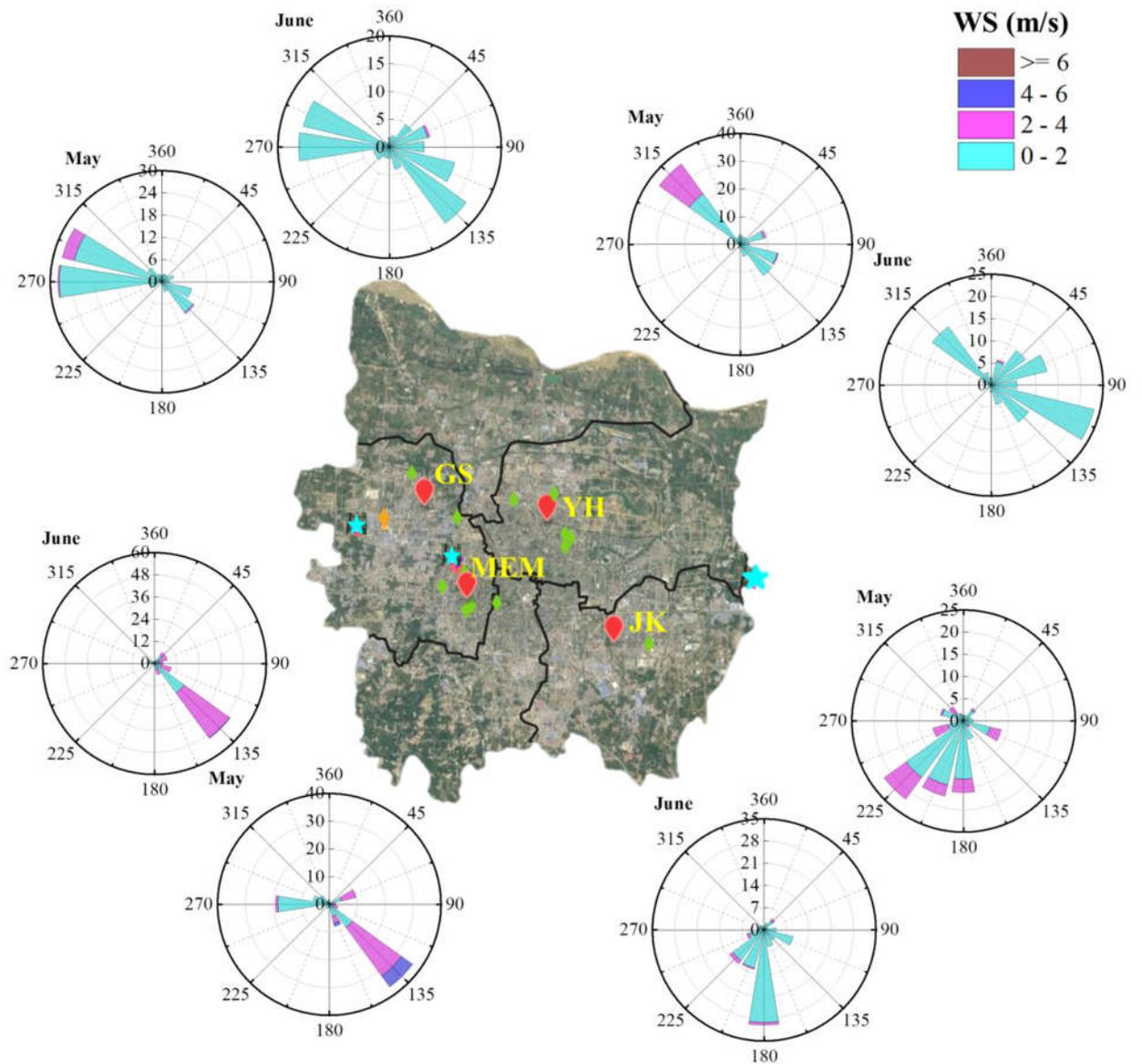
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Fig.2 Wind direction for each site during May to September, 2017



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Fig. 3 Cluster analysis of Zhengzhou in each sampling month



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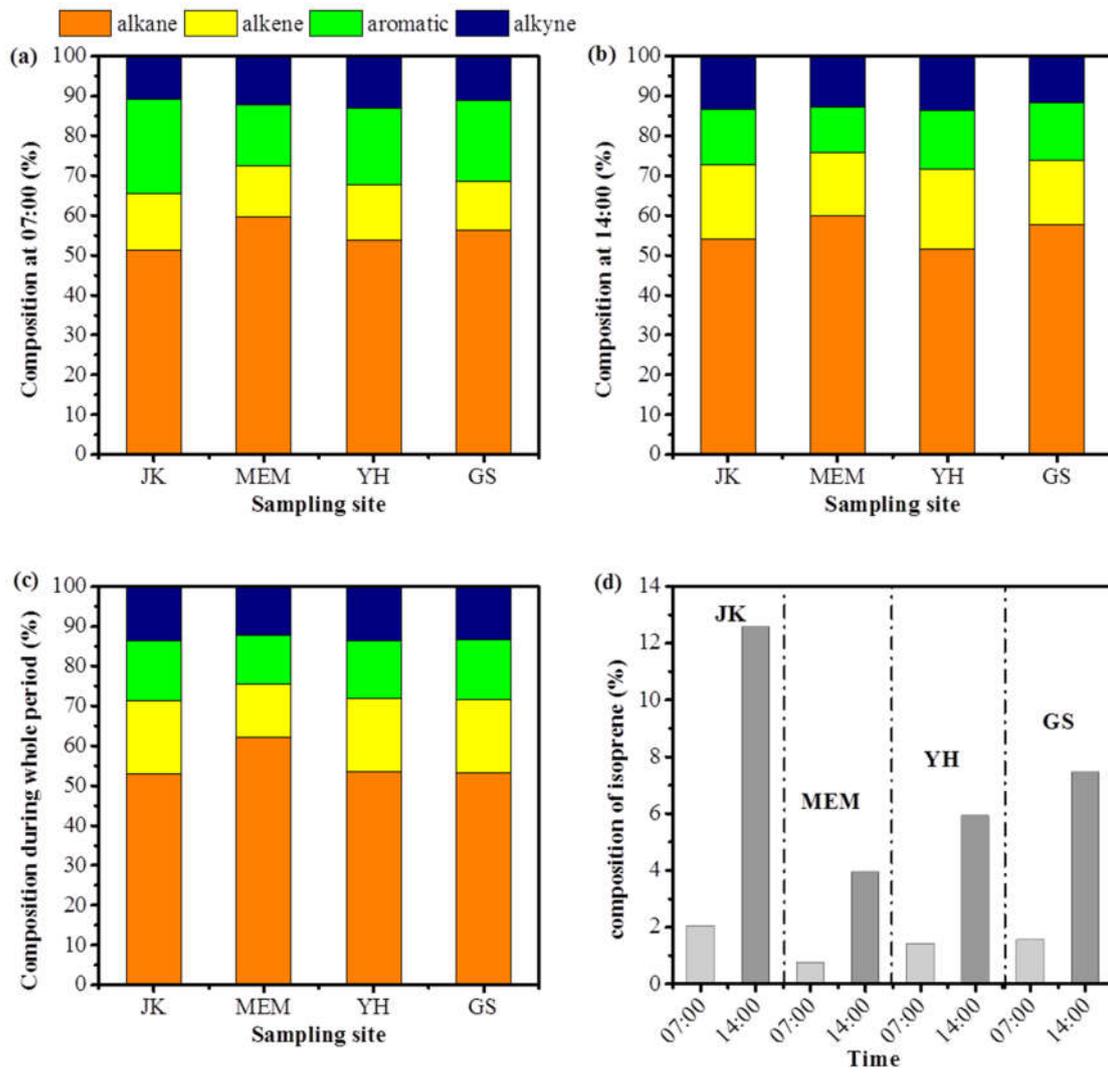
1912 Fig.4 Wind rose at each site in May and June (the wind distribution in other three months were

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illustrated in Fig S2)

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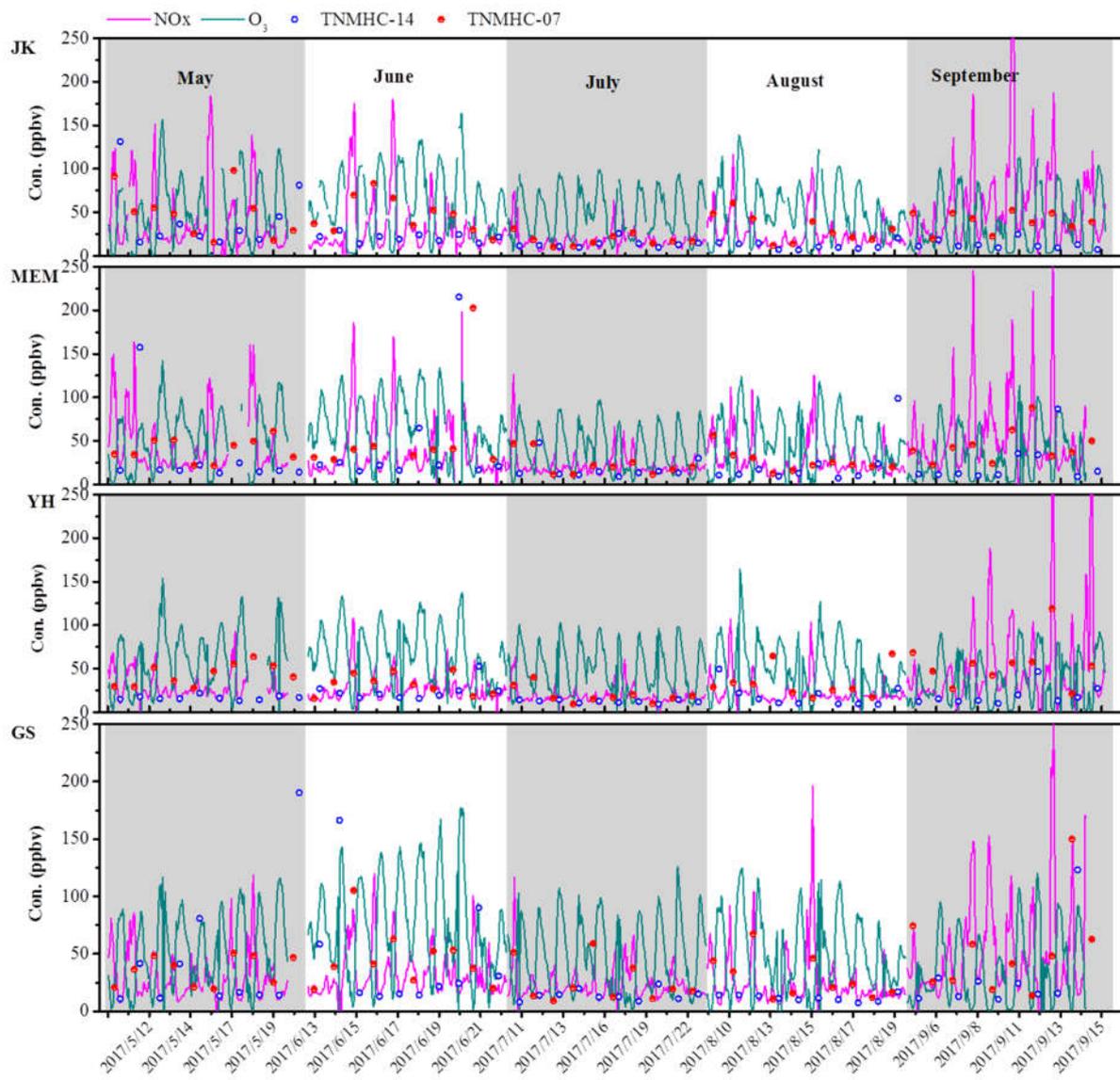
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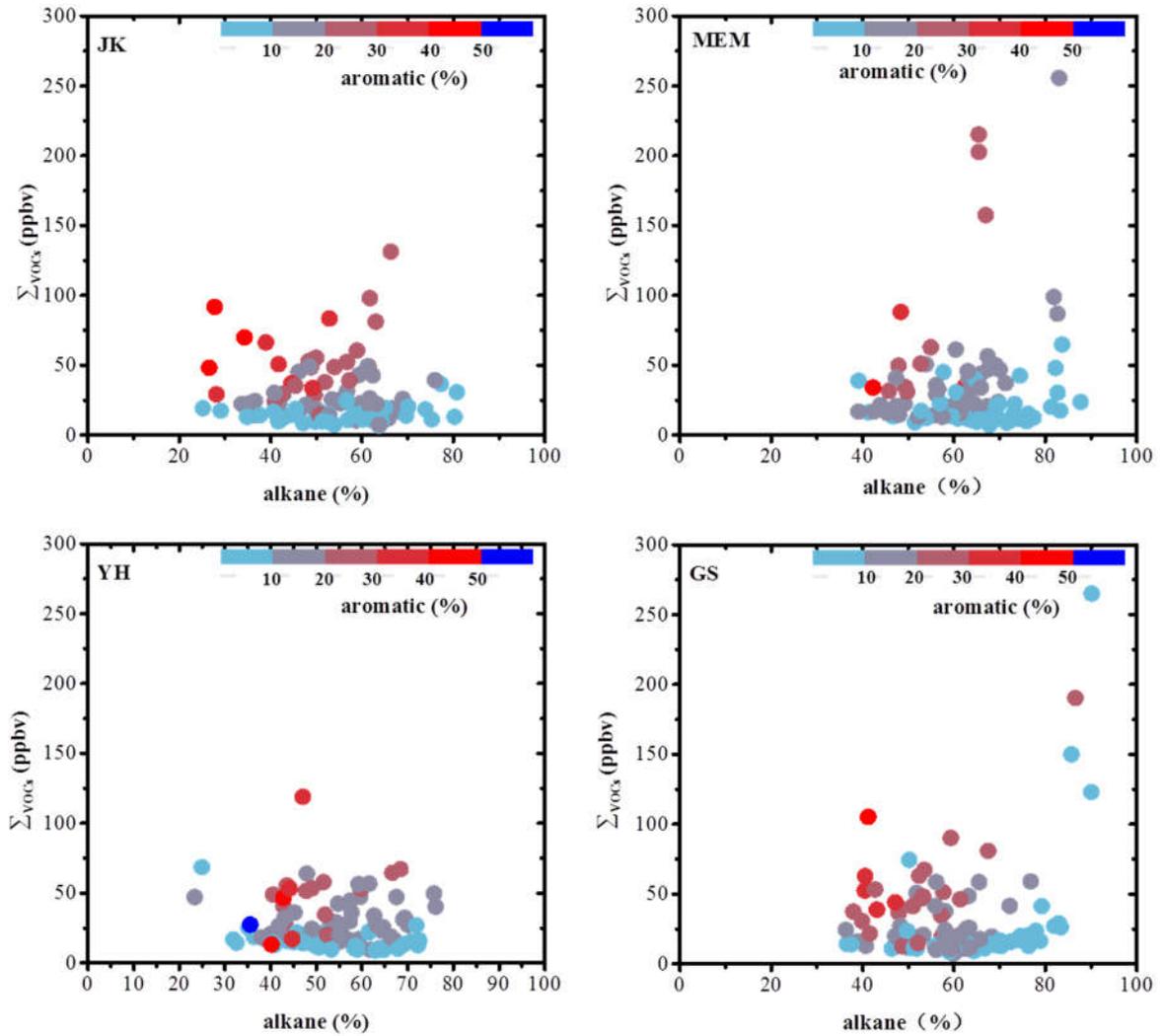
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Fig. 5 Compositions of major organic classes at 07:00 LT (a), 14:00 LT (b) and during the whole sampling period (c) at the four sites, and the composition of isoprene at 07:00 LT and 14:00 LT for each site (d).



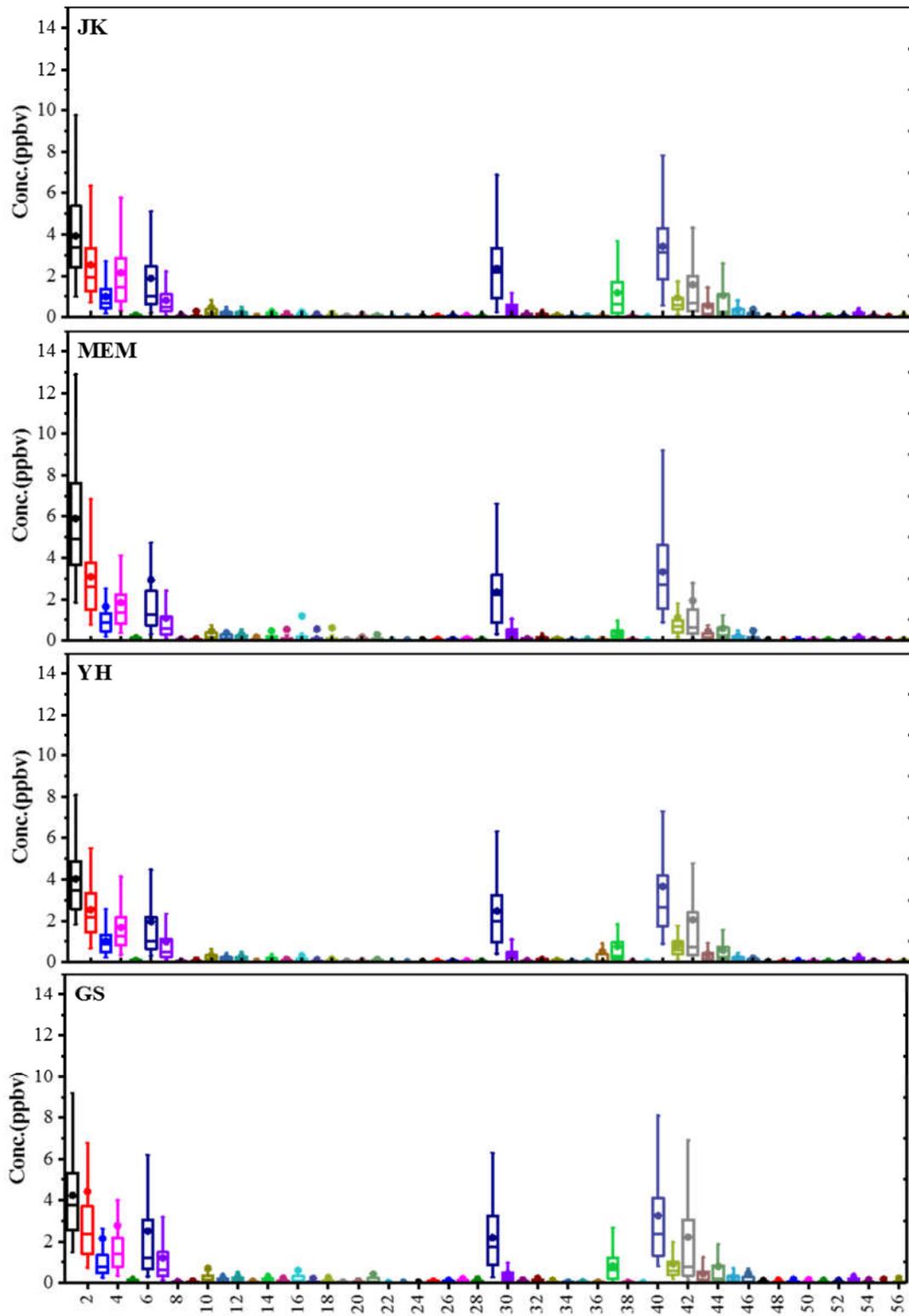
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Fig.6 Temporal variations of mixing ratios of  $\Sigma$  VOCs, NO<sub>x</sub> and O<sub>3</sub> at the four sites during the whole sampling period, in which  $\Sigma$  VOCs-07 stands for the concentration level of  $\Sigma$  VOCs observed at 07:00 LT, and  $\Sigma$  VOCs-14 was that observed at 14:00 LT.



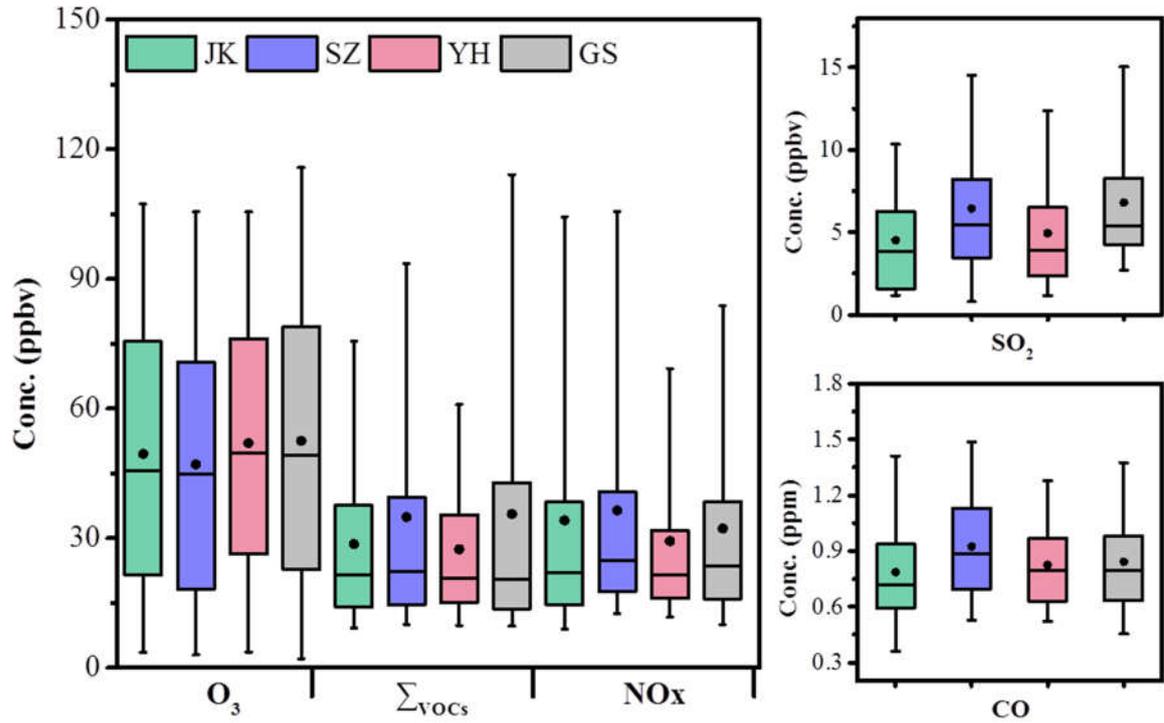
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Fig. 7 The relationship between mixing ratio of  $\Sigma$  VOCs and the composition of alkane, the data points were color coded with the composition of aromatic.



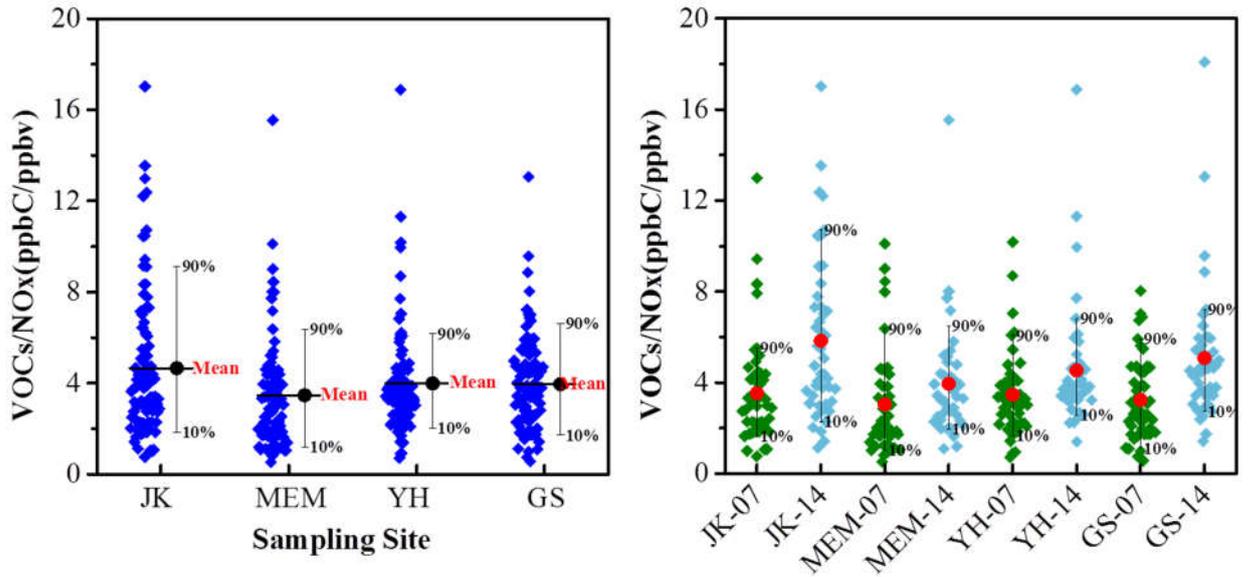
1931

1932 Fig.8 Concentrations of 57 VOCs at each site for the whole sampling period, the whisker was  
 1933 ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in  
 1934 the box represent median value. The number of chemicals can refer from Table S1.



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Fig. 9 The distribution of concentration point on O<sub>3</sub>, ΣVOCs, NO<sub>x</sub>, SO<sub>2</sub> and CO at each site, the range of the box was 25%-75%, the black line in the box stands for median level, the black dot represent the average level, the range of whisker was 5-95%.

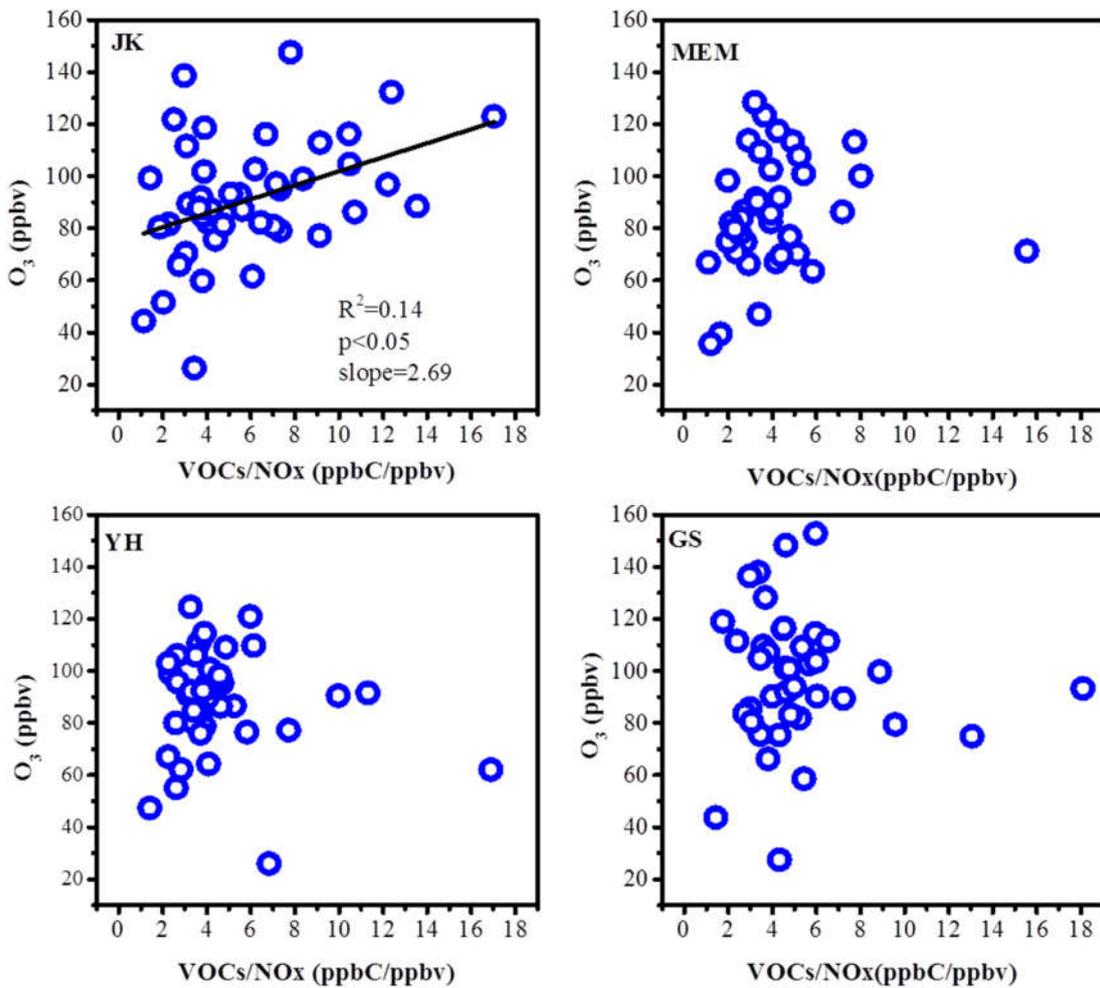


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Fig.10 The data distribution of VOCs/NOx(ppbC/ppbv) at the four sites (left), and the ratio observed at 07:00 LT and 14:00 LT were presented (right).



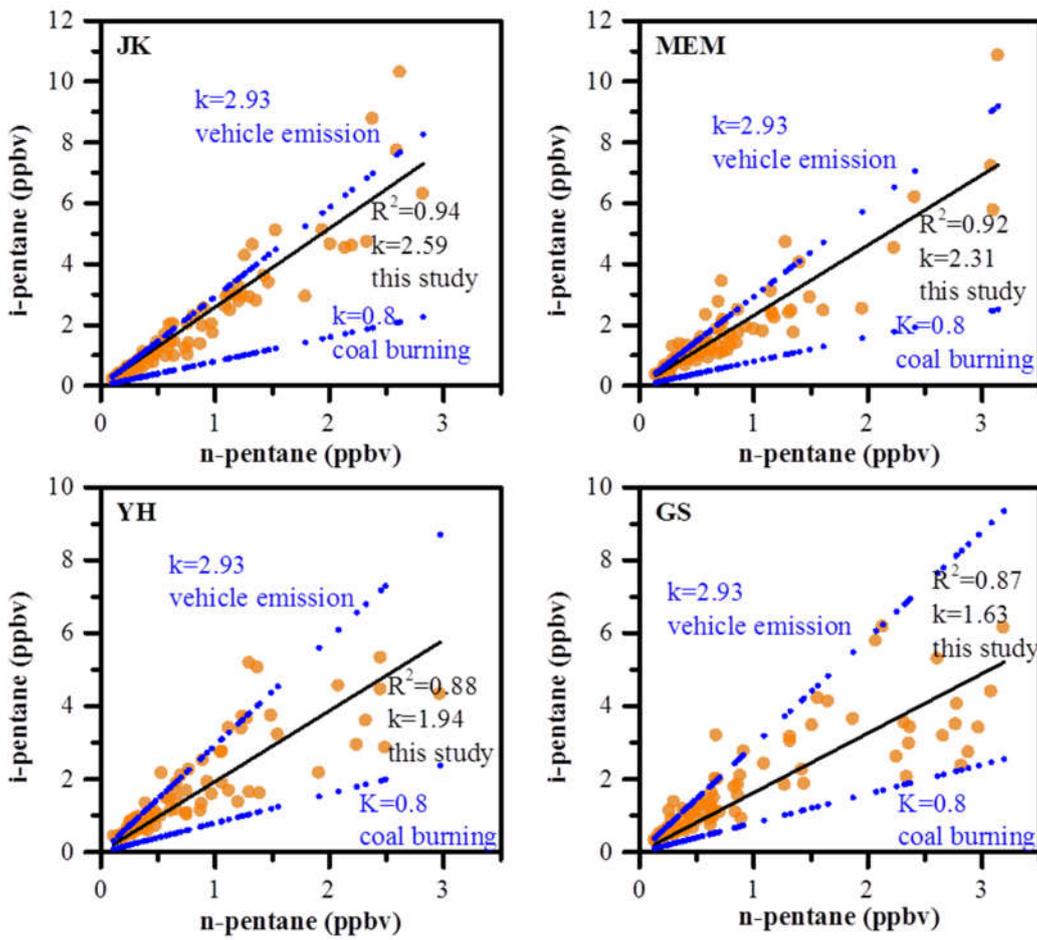
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Fig.11 The relationship between O3 and VOCs/NOx at 14:00 LT

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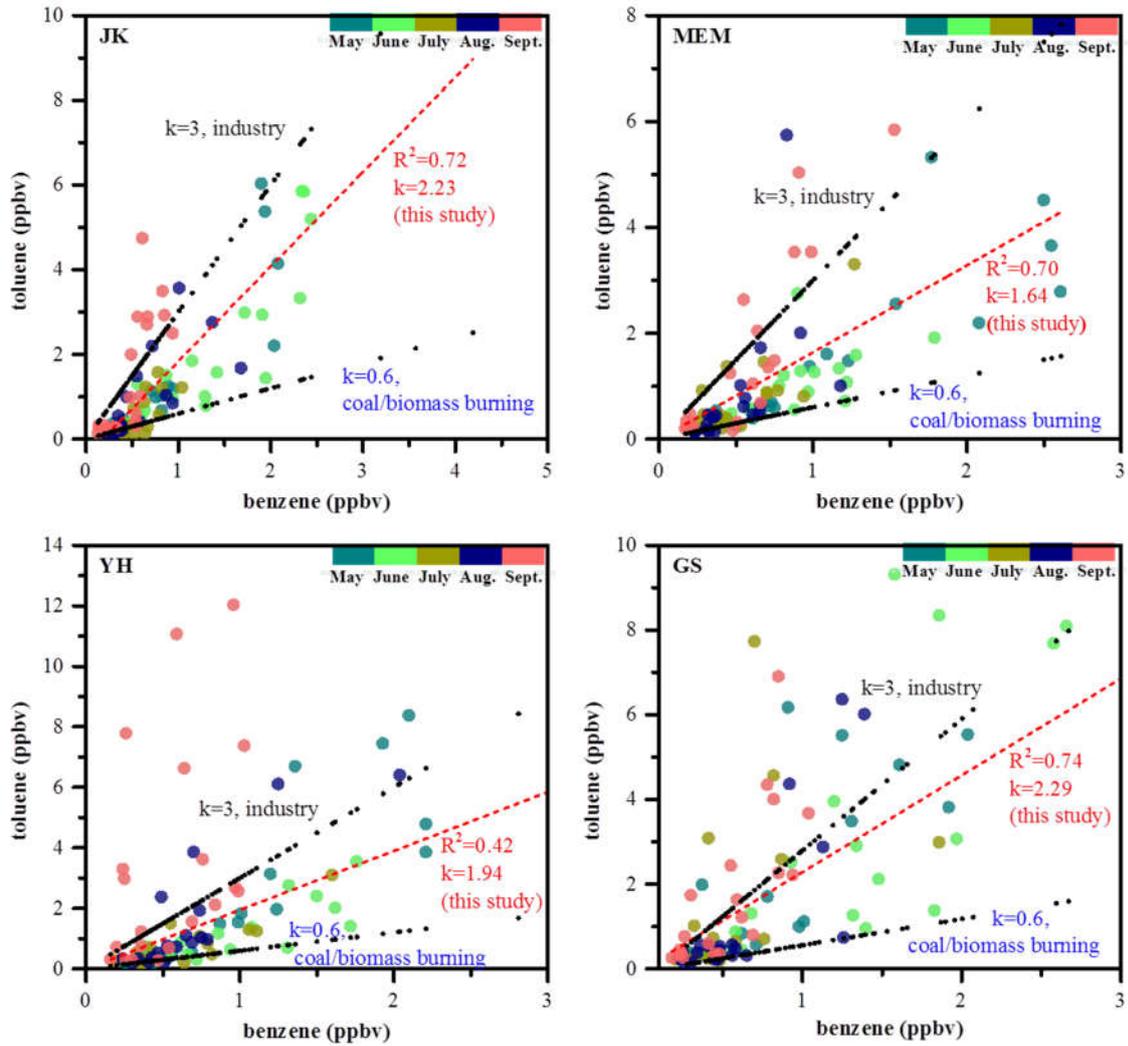
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Fig. 12 Ratios of isopentane to n-pentane at every site



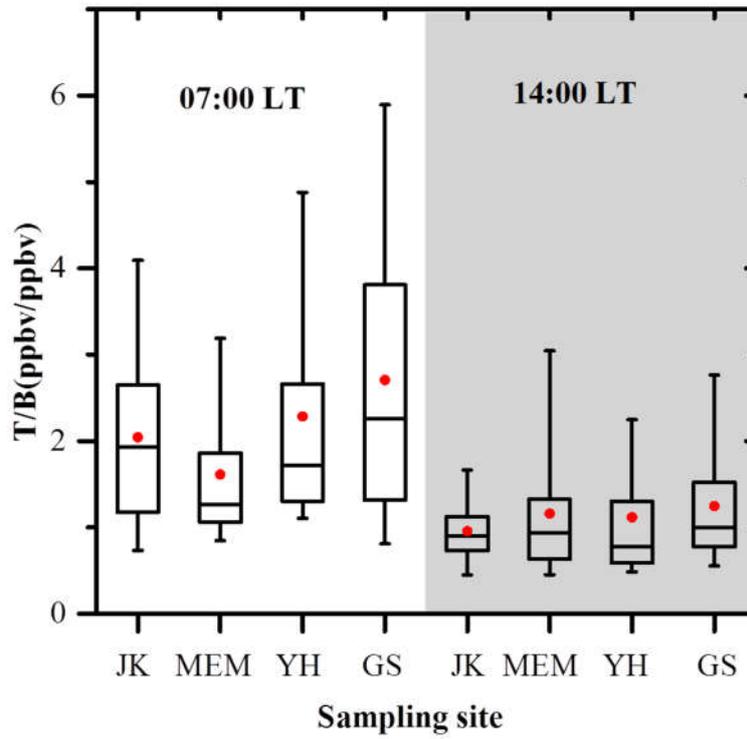
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1952 Fig.13 T/B ratios and linear correlation coefficients ( $R^2$ ) between benzene and toluene at every site,  
 1953 the data points were color mapped with sampling period.

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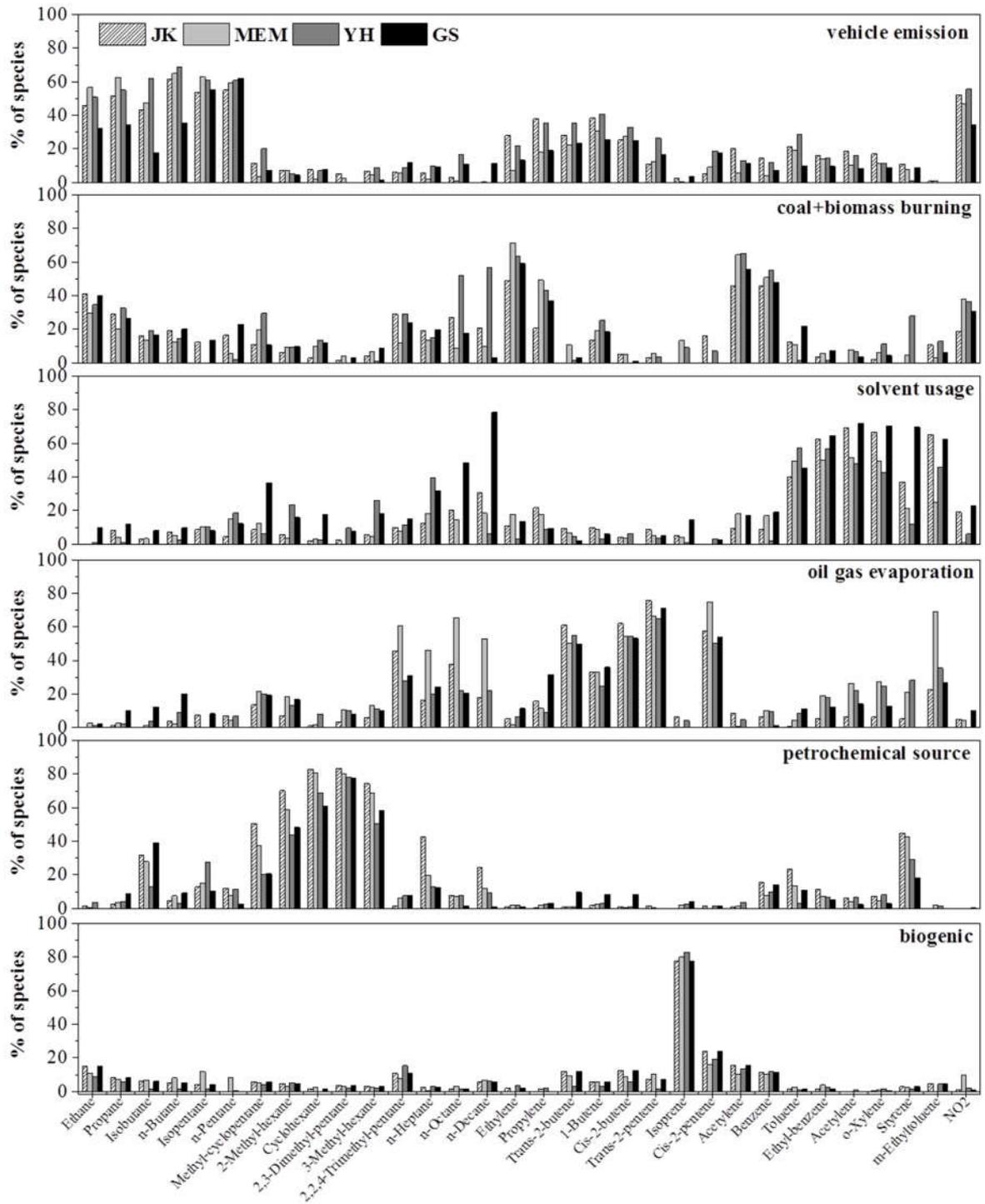
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1958 Fig. 14 The average ratio of T/B at 07:00LT and 14:00LT for each site during the whole sampling  
1959 period

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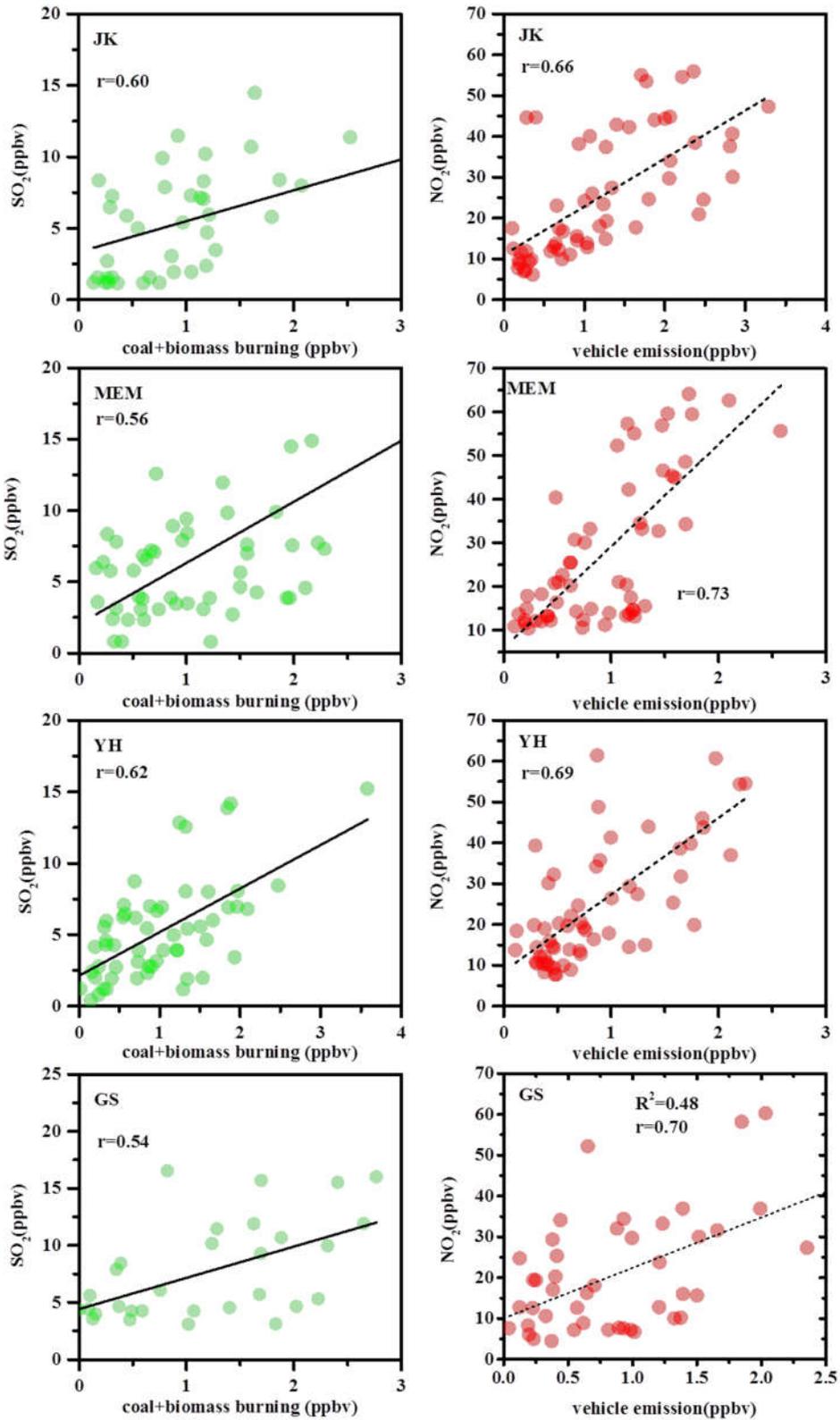
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Fig. 15 Explained variations in source profiles as identified by PMF



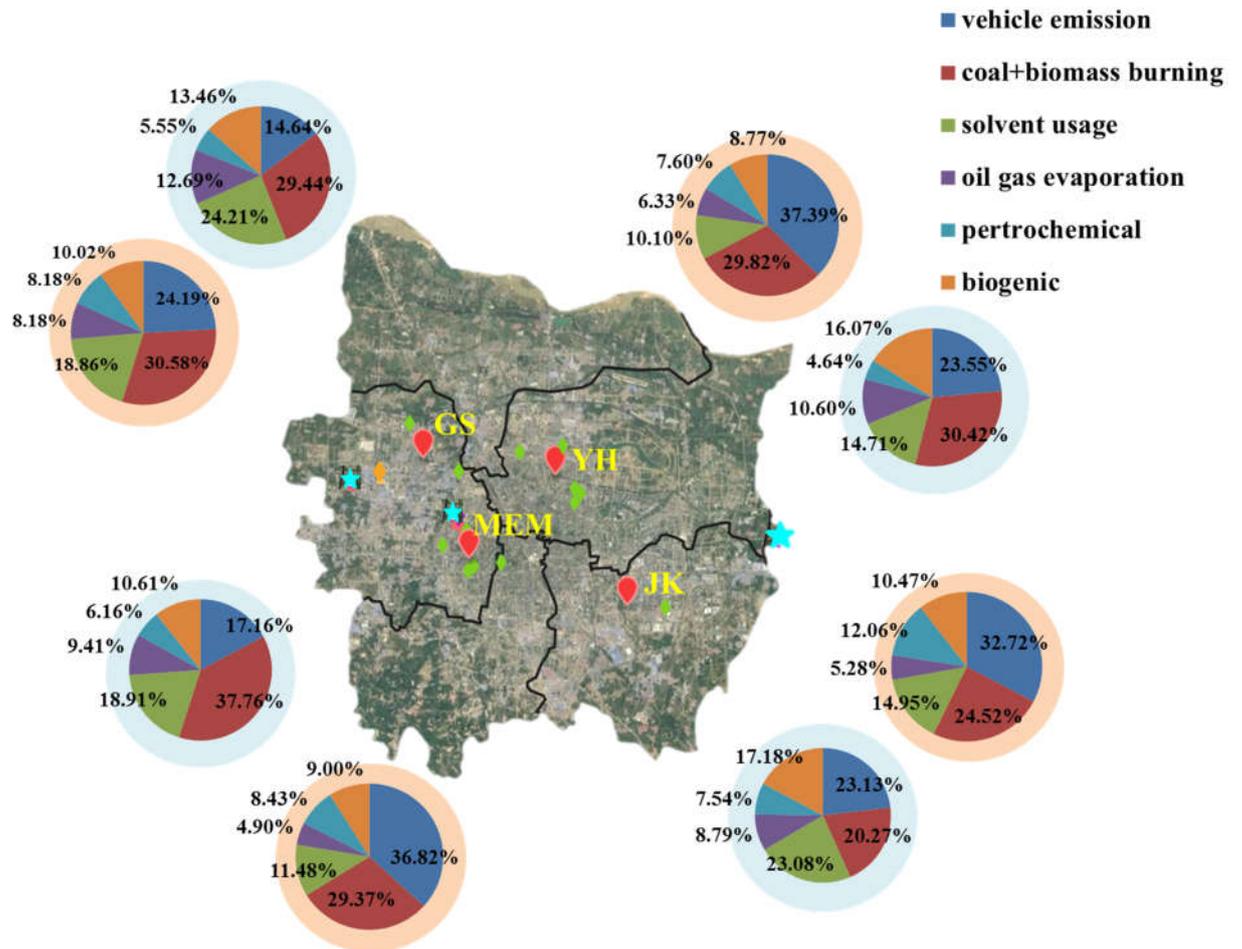
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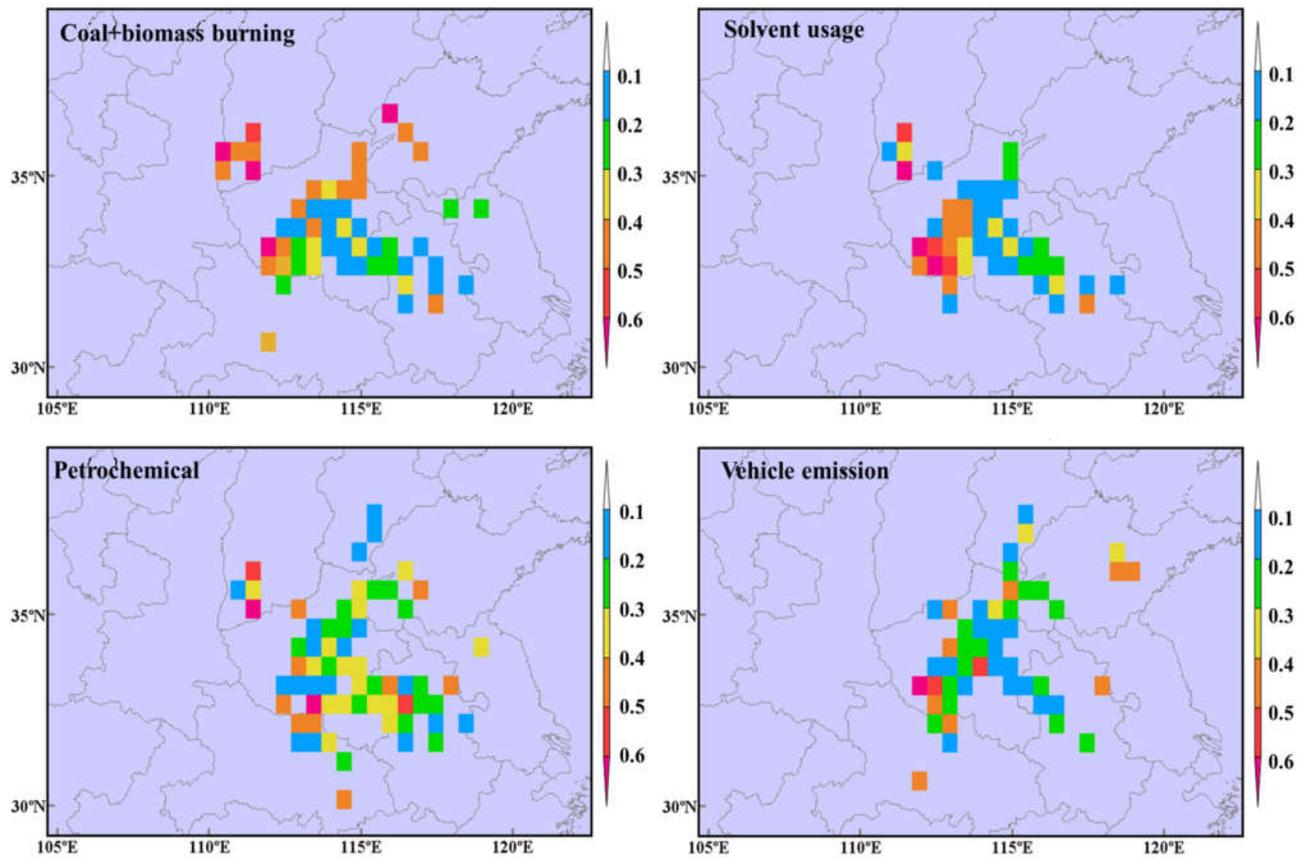
Fig. 16 Correlation analysis between contributions of coal+biomass burning and SO<sub>2</sub>, and vehicle emission and NO<sub>2</sub>



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Fig. 17 Source apportionment results during the whole sampling period. The results weighted in observed concentrations were shadowed with pink color, and the results estimated based on OFP were shadowed with light blue color.

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Fig. 18 Probable source regions apportioned by PSCF at Zhengzhou at summer (June-Aug. 2017) during sampling period

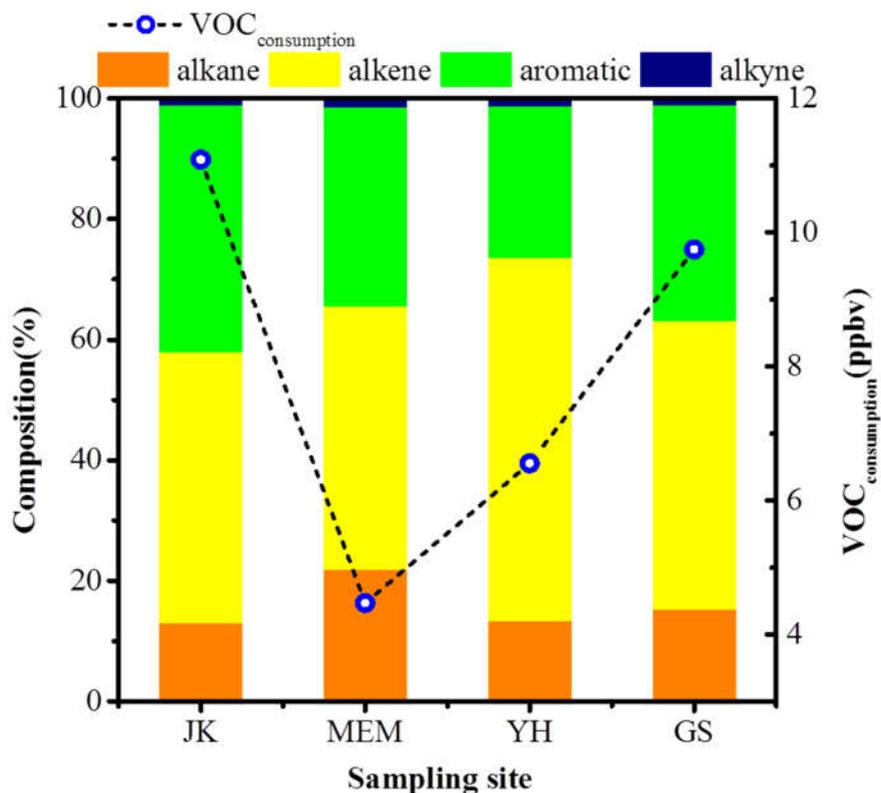


Fig. 19 The composition of major groups based on chemical consumption and the total consumption at each site.

1983

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### 1987 Supporting information

1988 Supplement materials has been added

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2026 **Marked manuscript**

2027 **Characterization of VOCs and their related atmospheric processes in a central**

2028 **China city during severe ozone pollution periods**

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2041 **Abstract**

2042 A five-month campaign (from May to September 2017) was conducted to  
2043 characterize volatile organic compounds (VOCs) for the first time at four sites in  
2044 Zhengzhou City, Henan Province, China, where ozone (O<sub>3</sub>) concentration has shown  
2045 an increasing trend in recent years. Canister samples were collected for measurement  
2046 of fifty-seven VOCs, which are the most important O<sub>3</sub> precursors. During the same  
2047 period, O<sub>3</sub> and its precursor gases were monitored online simultaneously. The results  
2048 indicated that the average mixing ratio of total quantified VOCs ( $\Sigma_{\text{VOCs}}$ , 28.83±22.05  
2049 ppbv) in Zhengzhou was lower than that in the other Chinese megacities, while alkyne  
2050 was in a higher proportion. The abundances, compositions and ratios of typical VOCs  
2051 showed clear spatial and temporal variations. The cluster analysis points out that air  
2052 masses from cities south of Zhengzhou were cleaner than from other directions.  
2053 Besides, the molar ratio of VOCs to NO<sub>x</sub> indicated that VOCs were more sensitive  
2054 than NO<sub>x</sub> to the O<sub>3</sub> formation in Zhengzhou. Meanwhile, the overall results further  
2055 implied that photochemical reactions at marginal sites where highly distributed with  
2056 industries were more efficient than those at other sites. The source apportionment  
2057 was conducted with Positive Matrix Factorization (PMF), and it was found that  
2058 vehicle exhaust, coal and biomass burning, and solvent usage were the major sources  
2059 for ambient VOCs at all four sites. From Potential Source Contribution Function  
2060 (PSCF) analysis, the strong emissions from coal+biomass burning and solvent usage  
2061 were concentrated in southwest of Shanxi and Henan province. The results of this  
2062 study gather scientific evidences on the pollution sources for Zhengzhou city,  
2063 benefiting the Government to establish efficient environmental control measures  
2064 particularly for O<sub>3</sub> pollution.

2065

2066 **1. Introduction**

2067 Volatile organic compounds (VOCs) are diverse and reactive chemicals. Vehicle  
2068 exhausts, fuel combustion and evaporation, and solvent usage are the known major  
2069 anthropogenic sources of VOCs (Zhang et al., 2014;Liu et al., 2017;Sahu et al., 2017).  
2070 VOCs play a crucial role in the ground-level ozone (O<sub>3</sub>) pollution, which has troubled

2071 many rapid economy-growth urban cities (Wang et al., 2017b;Nagashima et al.,  
2072 2017). Many related studies are thus being conducted globally (Wei et al.,  
2073 2014;Malley et al., 2015;Ou et al., 2015). In China, the investigations on VOCs  
2074 including source apportionment, measurement of emission profiles and interpretation  
2075 of seasonal variations were mainly concentrated in Yangtze River Delta (YRD), Pearl  
2076 River Delta (PRD) and Beijing-Tianjin (BJT) regions (An et al., 2014;Wang et al.,  
2077 2014;Chen et al., 2014;Liu et al., 2016;Guo et al., 2017). Limited studies have been  
2078 conducted in less developed or developing regions (i.e., southwestern and  
2079 northwestern China) where prominently impacted by biomass burning and with high  
2080 abundances of toxic and reactive compounds (Li et al., 2014;Li et al., 2017a).

2081 Fifty-seven VOCs, including C<sub>2</sub> - C<sub>10</sub> alkanes, alkenes, alkynes and aromatics,  
2082 which greatly contribute to ambient O<sub>3</sub> formation, have been identified and are  
2083 regularly monitored by Photochemical Assessment Monitoring Stations (PAMS)  
2084 (Shao et al., 2016;Chen et al., 2010). Due to characteristic structure and reactivity of  
2085 these compounds, their contributions in O<sub>3</sub> production were varied accordingly, and it  
2086 is reported that aromatics and alkenes were responsible for most of the weighted  
2087 reactivity of VOCs (59.4% and 25.8%, respectively) in Pearl River Delta (PRD)  
2088 region in China (Ou et al., 2015). Consequently, researchers have deduced that  
2089 reductions of alkenes and aromatics are profit for O<sub>3</sub> control (Carter, 1994). In  
2090 addition, with the variations on energy structure, industrial construction and  
2091 meteorological conditions (Wang et al., 2015;Shao et al., 2011), major emission  
2092 sources of VOCs at each city are unique. In less developed cities of Heilongjiang and  
2093 Anhui, biomass combustion had the highest contribution (40% and 36%, respectively)  
2094 to the O<sub>3</sub> formation potentials due to high quantity of agricultural activities, while in  
2095 the developed cities such as Shanghai, Beijing and Zhejiang, solvent usage has  
2096 become more dominant (>20%) than other pollution sources (Wu and Xie, 2017).  
2097 Therefore, identification on district emission sources of VOCs is necessary to provide  
2098 scientific-based information for policy-makers who establish efficient strategies to  
2099 alleviate O<sub>3</sub> pollution.

2100 In addition to the factors discussed above, non-linear relationships between

2101 ambient VOCs, nitrogen oxide (NO<sub>x</sub>) and O<sub>3</sub> production indicate that the reduction in  
2102 tropospheric O<sub>3</sub> is more complex than expected (Lin et al., 1998;Hidy and Blanchard,  
2103 2015;Li et al., 2018). Many modeling and field studies showed that photochemical O<sub>3</sub>  
2104 production in several cities in China such as Guangzhou, Shanghai and Beijing with  
2105 high levels of NO<sub>x</sub> were highly sensitive to VOCs (Shao et al., 2009;Gao et al.,  
2106 2017;Ou et al., 2016). The sensitivity regime is always varied with time and  
2107 geographical locations (Luecken et al., 2018). The percentage of VOC-limited regime  
2108 in North China Plain (NCP) increased from 4% to 6% between 2005-2013, owing to  
2109 the rapid increases of NO<sub>x</sub> emissions (Jin and Holloway, 2015).

2110 Zhengzhou City is an important developing city in the mid-west of the  
2111 Huanghe-Huaihe river flood plain in China. As the capital city of Henan Province, it  
2112 is densely populated with more than seven million residents in 2010 (Geng et al.,  
2113 2013). With the rapid growth of industrial activities, as well as increased vehicle  
2114 emissions and fuel combustions, air quality in Zhengzhou has notoriously deteriorated.  
2115 The Air quality index (AQI) for 65% of the days in 2013 exceeded the allowable  
2116 limits of 100 established by the Air Quality Guideline. Particularly, O<sub>3</sub> was the major  
2117 pollutant in summer and over 50% of the days in a year, the mixing ratio of O<sub>3</sub>  
2118 exceeded the Grade I standard (100 μg m<sup>-3</sup>) of daily maximum average 8-hour  
2119 (DMA8) in Henan (Shen et al., 2017;Gong et al., 2017). As one of the major  
2120 precursors of O<sub>3</sub>, the study on VOCs is of significance for Zhengzhou, since no  
2121 related researches are published in peer-reviewed literature. In this work, a  
2122 comprehensive sampling campaign for VOCs measurement and characterization has  
2123 been conducted at four monitoring stations during the time period of May - September  
2124 2017. The spatial and temporal variations in VOCs in Zhengzhou were determined.  
2125 The contributions of major emission sources were quantified, and the relationship  
2126 among O<sub>3</sub>-VOCs-NO<sub>x</sub> was discussed in details. The results and implications from this  
2127 study can provide useful guidance for policy-makers to alleviate ozone pollution in  
2128 Zhengzhou, China.

## 2129 **2. Observation and Methodology**

### 2130 **2.1 Sampling site**

2131 Based on the density of population distribution, locations of industrial facilities,  
2132 and the prevailing winds, four sites have been selected for sample collection: Jingkai  
2133 community (JK; 113.73°E, 34.72°N), municipal environmental monitoring station  
2134 (MEM; 113.61°E, 34.75°N), Yinhang school (YH; 113.68°E, 34.80°N) and Gongshui  
2135 company (GS; 113.57°E, 34.81°N), which are located at the southeastern,  
2136 southwestern, northeastern and northwestern of Zhengzhou, respectively (Fig. 1).  
2137 There is a main airport highway and heavy-traffic ring roads approximately 500 m  
2138 west of JK. Furthermore, the site is at a distance of 2 km from an industrial area,  
2139 which involves packaging and printing plants, and material distribution factories. It is  
2140 noteworthy that there were three coal-fired power plants in the urban area of  
2141 Zhengzhou city. One of the power plants with the highest production was 1.6 km  
2142 northwest of MEM. Both the MEM and YH include a mix of commercial and  
2143 condensed residential areas, whereas the apartments around YH are more aged. The  
2144 GS site is surrounded by several manufacturing plants, including pharmaceuticals,  
2145 materials, foods and machineries.

2146 Ten sampling days with the rainfall record (*ca.* 0 mm) were chosen in every  
2147 month during the period of May - September, 2017 consequently, to represent a  
2148 typical air quality condition in a month. Grab samples were collected minute using 3.2  
2149 L stainless-steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA), which  
2150 were pre-cleaned with high purity nitrogen and pressurized to 20 psi. Two samples,  
2151 one collected at 07:00 with increasing of human activities and another one collected at  
2152 14:00 with well-mixed of ambient air, were obtained on each sampling day. There was  
2153 a total of 400 samples collected in this study. The chemical analysis was  
2154 accomplished within two weeks after the collection of samples. Real-time data for  
2155 trace gases, including SO<sub>2</sub>, CO, NO<sub>2</sub> and O<sub>3</sub>, and synchronous meteorological data,  
2156 such as temperature (T), relative humidity (RH), wind direction (WD) and wind speed  
2157 (WS), were recorded at each air monitoring station.

## 2158 **2.2 Chemical Analysis**

2159 In this study, the measurement of VOCs was based on Compendium Method  
2160 TO-15, which was established by U.S. EPA. Air in the canister was concentrated

2161 using liquid-nitrogen at -160 °C in a cryogenic pre-concentrator (7100A, Entech  
2162 Instrument, Inc.). Both the CO<sub>2</sub> and H<sub>2</sub>O were removed from the transfer line. The air  
2163 was then thermally desorbed at 120 °C and transferred for analysis to a gas  
2164 chromatography (GC, 7890A, Agilent Technologies, Santa Clara, CA, USA) coupled  
2165 with dual detectors, i.e. a mass spectrometric detector (MSD) and a flame ionization  
2166 detector (FID) (5977E, Agilent Technology). Dual columns were applied for the  
2167 simultaneous analysis of C<sub>2</sub> - C<sub>11</sub> hydrocarbons. A PLOT column (15 m, internal  
2168 diameter of 0.32 mm and film thickness of 3.0 μm) was connected to the FID for  
2169 detection of C<sub>2</sub> - C<sub>5</sub> NMHCs, whereas C<sub>5</sub> - C<sub>10</sub> NMHCs, oxygenated VOCs (OVOCs)  
2170 and halocarbons were separated using a DB-624 column (30 m×0.25 mm inner  
2171 diameter × 3.0 μm film thickness), which was connected to the MSD. Target  
2172 compounds were identified with retention time and mass spectra, and quantified with  
2173 multi-point calibration curve in this study. The standard gas of PAMS (1 ppm; Spectra  
2174 Gases Inc, NJ, USA) was used to construct the calibration curves for the 57 target  
2175 VOCs, including 28 alkanes, 11 alkenes, acetylene and 17 aromatics. Detailed  
2176 information on the target analyses involved in this study and their corresponding  
2177 linearity of calibration (R<sup>2</sup>), measurement relative standard deviation (RSD), method  
2178 detection limit (MDL), maximum increment reactivity (MIR, carter, 2010) are  
2179 presented in Table S1.

### 2180 **2.3 Positive matrix factorization (PMF)**

2181 The U.S. EPA PMF 5.0 software was used for source apportionment (Lau et al.,  
2182 2010;Abeleira et al., 2017;Xue et al., 2017). Due to the complex chemical reactions,  
2183 the application of PMF in VOCs has to be based on a couple of principles: eliminating  
2184 species with mixing ratios below MDL and excluding species with high reactivity,  
2185 except for the source markers (Shao et al., 2016;Guo et al., 2011). Finally, 31 VOC  
2186 species and NO<sub>2</sub> were chosen for the source apportionment analysis.

2187 In this study, PMF was performed with fifty base runs for each site, results with  
2188 the minimum Q value (a parameter used to express uncertainties of PMF results) were  
2189 considered as optimum solutions. In Table S2 the r<sup>2</sup> between observed values and  
2190 predicted values of selected VOCs and NO<sub>2</sub> are presented for the four sites, the r<sup>2</sup> for

2191 most species (>80%) were higher than 0.6, compounds with  $r^2 < 0.6$  were down  
2192 weighted when determine factor sources.

2193 During PMF analysis, bootstrap method was used to evaluate stability and  
2194 uncertainty of the base run solution, setting the minimum correlation R-value at 0.6,  
2195 100 bootstrap runs were performed, and the results were showing in Table S3, and  
2196 acceptable results (>80%) were gained for all the factors.

2197 Three to nine factors were selected to initiate the running of PMF, the Q/Q(exp)  
2198 for every site at fixed factor size were presented in Table S4. With the increase of  
2199 factor number, the ratios Q/Q(exp) were declined due to additional factors. When the  
2200 factor size changing from 3 to 4, 4 to 5, and 5 to 6, the decrement of Q/Q(exp) were  
2201 larger (~18-25%), while the change was lower than 12% after factors increased to 7,  
2202 combined with the field conditions, six factors were defined at each site.

#### 2203 **2.4 Potential source contribution function (PSCF)**

2204 In this study, the probability of air clusters with source concentration higher than  
2205 a certain value was estimated (Hopke et al., 1995). Briefly, the PSCF value in  $ij^{\text{th}}$  grid  
2206 was the ratio of the number of endpoints with higher source concentration relative to  
2207 the total number of endpoints in  $ij^{\text{th}}$  grid cell. The criterion value, equal to 75<sup>th</sup>  
2208 percentile of the targeted source concentration in this study, was used to verdict  
2209 whether the value was higher or not. The 48-hour back trajectories was calculated  
2210 with Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model.  
2211 While there are many grid cells with small values, which could result in high  
2212 uncertainty, the weight function ( $W_{ij}$ ) was introduced to gain optimized PSCF results  
2213 (WPSCF) (Polissar et al., 1999). According to average values of end points in each  
2214 cell, in this case,  $W_{ij}$  was presented as below.

$$W_{ij} = \begin{cases} 1.0 & n_{ij} > 30 \\ 0.7 & 10 < n_{ij} \leq 30 \\ 0.42 & 5 < n_{ij} \leq 10 \\ 0.05 & n_{ij} \leq 5 \end{cases}$$

2215

#### 2216 **2.5 Estimation of the initial NO<sub>x</sub> and VOCs**

2217 With the assumption that chemical loss of NO<sub>x</sub> and VOCs were mainly due to  
2218 their reactions with hydroxyl radical (•OH), the initial mixing ratio of NO<sub>x</sub> can be  
2219 calculated with the equation as (Shiu et al., 2007;Shao et al., 2009):

$$2220 \quad [\text{NO}_x] = [\text{NO}_x]_0 \exp(-k [\bullet\text{OH}] \Delta t) \quad (1)$$

2221 where k stands for the reaction rate between NO<sub>x</sub> and [•OH]. In this study, k was set  
2222 as the observed average ratio of NO<sub>2</sub>/NO<sub>x</sub> during this campaign.

2223 The photochemical age Δt was usually displayed as the ratio between the two  
2224 compounds, which emitted from common source, but owning different reaction rate  
2225 with •OH. For this case, the photochemical age clock was performed with  
2226 ethylbenzene (E) and m,p-xylene (X) (Sun et al., 2016).

$$2227 \quad [\bullet\text{OH}] \Delta t = 1/(k_x - k_E) [\ln(C_X/C_E) - \ln(X_0/E_0)] \quad (2)$$

2228 which k<sub>x</sub> and k<sub>E</sub> represent their rate constants with •OH, C<sub>X</sub> and C<sub>E</sub> correspond to the  
2229 observed mixing ratios; X<sub>0</sub> and E<sub>0</sub> were their initial concentrations. The X<sub>0</sub>/E<sub>0</sub> was  
2230 prescribed at 5 percentile of the observed ratios at 07:00 in this paper.

2231 The initial mixing ratio of VOC was estimated with the method as NO<sub>x</sub> (Shiu et  
2232 al., 2007):

$$2233 \quad [\text{VOC}]_0 = [\text{VOC}]_t \exp(k_i [\bullet\text{OH}] \Delta t) \quad (3)$$

2234 where [VOC]<sub>t</sub> was the observed mixing ratio of i<sup>th</sup> species and k<sub>i</sub> was the  
2235 correspondent rate constant with •OH.

### 2236 **3 Results and discussions**

#### 2237 **3.1 Meteorological variations and Mixing ratios**

2238 Meteorological conditions are important factors that impact both the  
2239 compositions and levels of VOCs. During the sampling period, the T (RH) was varied  
2240 from 15°C (15%) to 38°C (100%) (Fig.S1), and the dominant wind was northwestern  
2241 and southeastern (Fig. 2). The air clusters, analyzed by HYSPLIT model, showed  
2242 moderate differences in each month (Fig. 3). In May, clusters arriving at Zhengzhou  
2243 demonstrated longer paths, and included six clusters in total, while in June, the length  
2244 of clusters were shorter. However, the concentration levels and compositions of VOCs  
2245 were similar in the two months. In May, the largest cluster (27.2%) was passed over  
2246 from Yinchuan, a central city in northwest China, then crossing several non-capital

2247 cities (i.e., Yanan, Yuncheng and Luoyang) in Shanxi and Sichuan provinces. Such a  
2248 long-range transport of pollutants might result a less impact on the air quality of  
2249 Zhengzhou, as comparable level and similar compositions of VOCs were obtained  
2250 during the period of May - June. In June, August and September, approximately half  
2251 of the air trajectories originated from the areas of Henan province, indicating the air  
2252 pollutants in Zhengzhou were impacted by local factors at most time.

2253 The total concentrations of VOCs ( $\Sigma_{\text{VOCs}}$ ) are presented in Table 1. The  $\Sigma_{\text{VOCs}}$   
2254 varied at the four sites, where the highest  $\Sigma_{\text{VOCs}}$  and their compositions were not  
2255 identical across the sampling months as well. In May 2017, the highest  $\Sigma_{\text{VOCs}}$  was  
2256 reported at JK ( $37.65 \pm 22.58$  ppbv), followed by GS ( $31.73 \pm 18.70$  ppbv), YH ( $30.05$   
2257  $\pm 16.43$  ppbv) and MEM ( $29.05 \pm 15.34$  ppbv), while the  $\Sigma_{\text{VOCs}}$  values for the month of  
2258 June, July, August and September were found to be in the order of:  
2259 GS>JK>MEM>YH, MEM>GS>JK>YH, YH>MEM>JK>GS, and MEM> YH >  
2260 GS >JK, respectively. This can be attributed to numerous factors that will be explored  
2261 later in the paper. Besides the emission sources (to be discussed in Section 3.2), the  
2262 impacts controlled by meteorological conditions should not be ignored as well. For  
2263 instance, the prevailing wind in May was northwestern at GS and YH, while the  
2264 southwestern wind was dominant at JK (Fig 4). The transport of air pollutants from  
2265 urban center and industrial plants should be resulted in the highest level of  $\Sigma_{\text{VOCs}}$  at JK.  
2266 In June 2017, the prevailing wind was southeastern at MEM, YH and GS (Fig. 4). The  
2267 average wind speed at GS ( $0.74 \pm 0.33$  m s<sup>-1</sup>) was lower than that at MEM ( $1.84 \pm$   
2268  $0.94$  m·s<sup>-1</sup>) and YH ( $0.97 \pm 0.36$  m s<sup>-1</sup>) (Table 2), indicating poor dispersion conditions  
2269 at GS. The air pollutants emitted from MEM and YH were more liable resulting in a  
2270 higher level of  $\Sigma_{\text{VOCs}}$  at GS in June. It should be noted that, when  $\Sigma_{\text{VOCs}}$  at JK was  
2271 higher than that of GS, the level at YH was higher than that of MEM, and vice versa.  
2272 Except for the discriminations between the pollution sources at every site, the above  
2273 phenomenon might be a result of the topography, where the elevation was gradually  
2274 increased from east to west in Zhengzhou (Mu et al., 2016).

2275 Due to the variations of the planet boundary layer (PBL) height, solar radiation  
2276 and emission sources, the concentrations of VOCs displayed obvious differences

2277 between morning and afternoon time (07:00LT and 14:00LT in this study). Compared  
2278 with morning period, the aromatic compounds showed lower compositions at 14:00 LT  
2279 (Fig. 5), because of the increased planet boundary layer and the active photochemical  
2280 reactions, while alkenes always peaked in the 14:00 LT. According to the dataset, the  
2281 increases in alkene compositions (~4.3% uplift) were mainly due to higher  
2282 contributions of isoprene (~1.4% at morning and 7.6% in the afternoon), which was  
2283 mainly emitted from biogenic sources and increased exponentially with ambient  
2284 temperature (Jiang et al., 2018).

2285 The average  $\Sigma_{\text{VOCs}}$  values in Zhengzhou ( $28.83 \pm 22.05$  ppbv) were significantly  
2286 lower than those in Beijing (65.55 ppbv), Hangzhou (55.9 ppbv), Guangzhou (47.3  
2287 ppbv) and Nanjing (43.5 ppbv), and higher than that in Wuhan ( $23.3 \pm 0.5$  ppbv)  
2288 (Table 3). Factors, including population density, industrial activity, fuel composition,  
2289 local stringent regulations for environmental protection, terrain, and weather are the  
2290 potential reasons for the discrimination of VOCs concentrations in those cities. With  
2291 regard to the weight percentage of major groups (Table 3), the composition of alkanes  
2292 was the largest in all cities because of their longer lifetimes and widespread from a  
2293 variety of pollution sources (Fig. 5), while the composition of aromatics was lower  
2294 than alkenes in these cities except for Guangzhou. It is well known that aromatics  
2295 mainly originate from solvent usage and vehicle exhaust in summer. The large amount  
2296 of shoemaking and shipbuilding industries involving large amounts of solvent usage  
2297 may be the main reason for the higher composition of aromatics in Guangzhou. In  
2298 comparison with other four cities, the composition of aromatics in Zhengzhou was the  
2299 lowest probably due to its less solvent-used manufacturers than in Guangzhou,  
2300 Hangzhou and Nanjing, and less numbers of vehicles than in Beijing. Alkyne  
2301 contributes least to VOCs in cities listed in Table 3, with higher level observed in  
2302 Zhengzhou, where ranked second after Hangzhou. Alkyne typically originates from  
2303 combustion sources. Zhu et al. (2016) observed that the composition of alkyne in the  
2304 biomass-burning period could be double of that in the non-biomass burning period  
2305 (Zhu et al., 2016). As Henan is the largest agricultural province in China and the  
2306 sampling duration covered the crop harvest season, the residents often used crop

2307 residues as the biofuel for their subsistence and a higher alkyne composition in  
2308 Zhengzhou was thus resulted.

### 2309 **3.2 Temporal variations**

2310 The time series of mixing ratios of  $\text{NO}_x$ ,  $\text{O}_3$  and  $\Sigma_{\text{VOCs}}$  at every site are shown in  
2311 Fig. 6. The results showed a distinctive temporal characteristic where lower levels of  
2312  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{O}_3$  and  $\Sigma_{\text{VOCs}}$  were observed in July and August (mid-summer) (Table  
2313 S5). These results were similar to those obtained for other urban areas (Li and Wang,  
2314 2012; Cheng et al., 1997; Na et al., 2001). Changes in PBL height, human activities,  
2315 and abundance of hydroxyl radicals ( $\bullet\text{OH}$ ) were the potential causes for the  
2316 phenomenon. Pal et al. (2012) reported that the PBL height was positively correlated  
2317 with temperature. The occurrences of precipitation and raining were also frequent in  
2318 most areas of China during summer, resulting in decreasing background level of air  
2319 pollutants. Additionally, a series of effective local policies, such as prohibition of  
2320 painting and coating in open air and limitations on fuel supply between 10:00 -17:00  
2321 LT during hot summer days assisted in suppressing the emissions of VOCs.  
2322 Meanwhile, many organizations, such as schools, institutes and scattered private  
2323 workshops, were closed due to summer vacations. Some large-scale industries also  
2324 stopped manufacturing processes for two weeks during this period. Consequently, the  
2325 anthropogenic emissions were reduced, which in turn resulted in a decrease in VOCs,  
2326  $\text{SO}_2$ , and  $\text{NO}_x$  emissions. The reduction of precursor levels and unfavorable  
2327 photochemical conditions (such as, higher RH) resulted in the lower  $\text{O}_3$  levels in July  
2328 and August.

2329 Beside local emissions, the long-range air mass also had some impacts on  
2330 relatively lower level of  $\Sigma_{\text{VOCs}}$  in July. As illustrated in Fig.3, different from other  
2331 months, the air current was originated with the largest portion (ca. 88.68%) of clusters  
2332 from Hubei province, where the average  $\Sigma_{\text{VOCs}}$  in its capital city ( $23.3\pm 0.6$  ppbv) (Lyu  
2333 et al., 2016) was lower than that in Zhengzhou ( $29.18\pm 23.08$  ppbv). In combination  
2334 with the lower weight percentage of photothermal-reactive aromatics ( $10.30\pm 4.23\%$ ),  
2335 and the lowest toluene to benzene (T/B) ratio of  $1.15\pm 0.99$  around this period, it is  
2336 possible that the cleaner air mass clusters originating from Hubei also contributed to

2337 the reduction of  $\Sigma_{\text{VOCs}}$  in July.

2338 As demonstrated in Fig. 6, the observed  $\Sigma_{\text{VOCs}}$  values at 07:00 LT were often  
2339 higher than those at 14:00 LT. The accumulation of pollutants during night-time and  
2340 the temperature inversion in the morning were the most reasonable explanations for  
2341 this phenomenon. Stronger photochemical reaction during noon-time led to the  
2342 reduction in atmospheric VOCs. It should be noted that pronounced  $\Sigma_{\text{VOCs}}$  were  
2343 occasionally observed at MEM and GS (Fig. 7), which were potentially ascribed to  
2344 sharp changes in local emissions and meteorological conditions. Specifically, at MEM,  
2345 the distinctive increment was always accompanied with obvious increases of alkanes  
2346 or aromatics (Fig. 7). Since the T and RH were often consistent during the sampling  
2347 period, the direct gas evaporations should be constant as well. Therefore, the  
2348 simultaneous increased concentrations of  $\text{SO}_2$ , CO and  $\text{NO}_x$  could illustrate the  
2349 potential impacts from combustion sources, such as emissions from nearby thermal  
2350 power plant. At GS, the increase of  $\Sigma_{\text{VOCs}}$  in June was usually with extremely high  
2351 levels of aromatics, due to the disturbance from solvent use for building renovation  
2352 during this period, and the abnormal high levels of  $\Sigma_{\text{VOCs}}$  in other months were related  
2353 to the rising concentrations of  $\text{C}_3$ - $\text{C}_4$  alkanes, which were mainly originated from  
2354 consumptions of compressed natural gas (CNG) or LPG (Huang et al., 2015). The  
2355 results support the possible impact from a gas-fueled power plant located about 1 km  
2356 southwest of the site (~18% of prevailing western wind at GS during May to  
2357 September).

2358 It is of interest to note that on the morning of 5th September, acetylene was  
2359 found in extremely high concentrations (14.65 - 39.42 ppbv). Its mixing ratio in most  
2360 of the urban areas was <10 ppbv (Louie et al., 2013; Duan et al., 2008; Guo et al.,  
2361 2012). It was learnt that the 5<sup>th</sup> September is a festival day for the people who worship  
2362 their ancestors. A large number of incenses and offerings, made up of wood and paper,  
2363 were burnt during the festival, resulting in an elevation of acetylene all over the  
2364 Zhengzhou city (Zhu et al., 2016).

### 2365 3.3 Spatial variations

2366 The  $\text{C}_2$  -  $\text{C}_5$  alkanes, acetylene, ethylene, toluene and benzene were the most

2367 abundant VOCs detected at all sites (Fig.8), and the mixing ratios of toluene varied  
2368 within a wide range at each site, because of its universal emission sources (e.g.,  
2369 vehicle exhaust emissions and solvent usage) (Wang et al., 2014;Barletta et al., 2005).  
2370 These chemicals contributed >60% for  $\Sigma_{\text{VOCs}}$  at each site, illustrating strong  
2371 combustion-related sources in Zhengzhou.

2372 Among the four major organic classes, alkane was the most abundant group as a  
2373 result of its widespread sources and longevity (Fig.5), accounted for 52.9%, 62.5%,  
2374 53.4%, 53.4% of the total  $\Sigma_{\text{VOCs}}$  at JK, MEM, GS, and YH, respectively. The highest  
2375 composition of alkane was observed at MEM due to the stronger contributions of  
2376 ethane, iso-pentane, and C<sub>6</sub>-C<sub>8</sub> branched alkanes (Fig. S3), which are emitted from  
2377 light-duty gasoline vehicles (Wang et al., 2017a).

2378 The average  $\Sigma_{\text{VOCs}}$  were slightly higher at industrially impacted sites of GS  
2379 ( $31.66 \pm 28.73$  ppbv) and JK ( $28.63 \pm 22.04$  ppbv) than those at MEM and YH (Fig.9).  
2380 Additionally, the air pollutants related to the combustion processes, such as SO<sub>2</sub> and  
2381 CO, were more abundant, though marginal, in western area of Zhengzhou (GS and  
2382 MEM) (Fig.9). Under high levels of VOCs and sufficient supply of NO<sub>x</sub>, the highest  
2383 average mixing ratio of O<sub>3</sub> was observed at GS, followed by YH where even with the  
2384 lowest VOCs and NO<sub>x</sub>, indicating that there are multiple factors, rather than the  
2385 absolute concentrations, contributed to the O<sub>3</sub> formation at YH.

2386 In June, the O<sub>3</sub> concentration often exceeded the national standard level of 80  
2387 ppbv, representing severe air pollution during this period. The average mixing ratio of  
2388 O<sub>3</sub> during daytime (07:00-18:00 LT) in June, 2017 at JK, MEM, YH, and GS were  
2389  $74.87 \pm 39.55$  ppbv,  $73.50 \pm 40.59$  ppbv,  $73.81 \pm 35.69$  ppbv, and  $87.99 \pm 46.11$  ppbv,  
2390 respectively (Table 4). The higher level of O<sub>3</sub> at GS was accompanied with the higher  
2391  $\Sigma_{\text{VOCs}}$  ( $39.29 \pm 25.37$  ppbv). The weight percentage of aromatics ( $15.62 \pm 12.06\%$ ) at  
2392 GS was higher than those at other sites as well, indicating that the painting and other  
2393 renovation activities at GS was potentially an important factor for its high O<sub>3</sub> level in  
2394 June. Even though both the  $\Sigma_{\text{VOCs}}$  and specifically high O<sub>3</sub> formation potential  
2395 compounds (such as alkenes and aromatics) at MEM were slightly higher than those  
2396 at YH (Table 4), the O<sub>3</sub> concentration at MEM was not higher. This could be attributed

2397 to other critical precursors such as NO. NO at MEM (7.72ppbv) was significantly  
2398 higher than that at YH (2.57 ppbv) during daytime, indicating that the titration  
2399 reaction between O<sub>3</sub> and NO was more efficient at MEM.

2400 It is well known that many O<sub>3</sub> episodes were attributable not only to local  
2401 sources but also to regional transports. For example, Streets et al. (2007) reported that  
2402 with continuous southern winds, the O<sub>3</sub> level in Beijing was 20-30% contributed from  
2403 its neighboring cities in Hebei. During this study, a typical regional ozone pollution  
2404 was happened on August 10<sup>th</sup> at YH (Fig.6). On that day, the ratios of  $\Sigma_{\text{VOCs}}/\text{NO}_x$  at  
2405 the four sites were all less than 6.5 (ppbC/ppbv) (Fig. S4), indicating a regional  
2406 VOC-control system, and that VOCs are the critical contributors to the formation of  
2407 O<sub>3</sub> in Zhengzhou. The reductions in  $\Sigma_{\text{VOCs}}$  in the afternoons (around 14:00 LT)  
2408 compared to mornings (around 07:00 LT) may have been caused from the uptake by  
2409 O<sub>3</sub> formation, while the reduction of  $\Sigma_{\text{VOCs}}$  and active compounds (i.e.,  
2410 aromatic+alkene) at 14:00 relative to 07:00, determined as 35% and 56% respectively,  
2411 were the least at YH among the four sites (Fig. S4). On the other hand, based on the  
2412 dispersion of wind direction, between 08:00 - 15:00 LT on August 10<sup>th</sup>, YH was at the  
2413 downwind position to the other three sites (Fig. S4). All of this confirmed that the  
2414 abnormally high O<sub>3</sub> at YH was caused by the transport of air pollutants from other  
2415 sites on that day.

### 2416 3.4 VOCs/NO<sub>x</sub> ratio

2417 The VOCs/NO<sub>x</sub> ratio is often used to distinguish whether a region is VOCs or  
2418 NO<sub>x</sub> limited in O<sub>3</sub> formation. According to the general case, the area was loaded in  
2419 VOC-sensitive regimes when VOCs/NO<sub>x</sub> ratios were lower than 10 in the morning;  
2420 and it would be on NO<sub>x</sub>-sensitive regime when VOCs/NO<sub>x</sub> ratios were greater than 20  
2421 (Sillman, 1999;Hanna et al., 1996). In this study, the mean value of VOCs /NO<sub>x</sub>  
2422 (ppbC/ppbv) were below 5 at all four sites (Fig.10), and 75% of the data points were  
2423 < 6, indicating that the O<sub>3</sub> formation was sensitive to VOCs in Zhengzhou, and the  
2424 reductions on the emissions of VOCs will be benefit for O<sub>3</sub> alleviation.

2425 The VOCs /NO<sub>x</sub> showed differences among the four sites (Fig. 10), with the  
2426 lowest value at MEM (~3.8) and the highest value at JK (~4.7). The distributions

2427 demonstrated that the production of O<sub>3</sub> at MEM was more sensitive to VOCs than JK  
2428 due to presence of emission from thermal-power plant. Meanwhile, approximately 14%  
2429 of the VOCs /NO<sub>x</sub> ratios of >8.0 were found in the NO<sub>x</sub>-limited site of JK, potentially  
2430 resulting from higher VOCs or lower NO<sub>x</sub> emissions than other sites. Both of the  
2431 mixing ratios and the statistical data showed higher levels of VOCs (with lower NO<sub>x</sub>)  
2432 at GS, where only ~4% of the ratios of > 8 was observed, indicating that there must be  
2433 other factors (unresolved in this study) impacted the variation of O<sub>3</sub> formation  
2434 regimes.

2435 From the daily variations of VOCs /NO<sub>x</sub> ratios (Fig. 10), higher values were  
2436 observed at 14:00 LT than 07:00 LT at the four sites, well correlated with less vehicle  
2437 emissions or more consumption paths for NO<sub>x</sub> with stronger light intensity. The  
2438 increment of VOCs /NO<sub>x</sub> at 14:00 LT was more obvious at JK and GS, suggesting that  
2439 more emission sources of VOCs at daytime, and resulting the O<sub>3</sub> formation system  
2440 shifting to the transition area in the afternoon.

2441 Many researches showed that the O<sub>3</sub> formation depends not only on the  
2442 abundances of precursors (mainly VOCs and NO<sub>x</sub>) and also VOCs to NO<sub>x</sub> ratio  
2443 (Pollack et al., 2013). In this research, the mixing ratio of O<sub>3</sub> at 14:00 LT presented a  
2444 slightly positive trend (p<0.05) with the uplift of VOCs /NO<sub>x</sub> at JK (Fig. 11),  
2445 consistent to the results observed at the megacity of Shanghai (Gao et al., 2017),  
2446 where the O<sub>3</sub> formation was more sensitive to NO<sub>x</sub> when high O<sub>3</sub> levels were  
2447 observed. This can be attributed to the increased O<sub>3</sub> production efficiency at high  
2448 VOCs /NO<sub>x</sub>. There were no discernible trends at other sites, possibly due to the  
2449 counteraction imposed by other uncertain factors.

### 2450 **3.5 Ratios of specific compounds**

2451 Ratios of specific VOCs are useful indicators to identify the emission sources  
2452 (Raysoni et al., 2017;Liu et al., 2015;Ho et al., 2009). In order to characterize the  
2453 differences in the contribution of various sources at each site, two ratios of  
2454 i-pentane/n-pentane and T/B ratios are discussed.

2455 The ratio of i-pentane to n-pentane can be used to differentiate potential sources  
2456 such as consumption of natural gas, vehicle emissions and fuel evaporations. It is

2457 claimed that in areas heavily impacted by natural gas drilling, the ratios were lied  
2458 within the range of 0.82 - 0.89 (Gilman et al., 2013;Abeleira et al., 2017). Higher  
2459 values were often reported for automobiles, in a range of 2.2 - 3.8 for vehicle  
2460 emissions, 1.8 - 4.6 for fuel evaporation, and 1.5 - 3.0 for gasoline (Russo et al.,  
2461 2010;McGaughey et al., 2004;Jobson et al., 2004;Wang et al., 2013), whereas the  
2462 ratios below unity was found for coal combustion (0.56 - 0.80) (Yan et al., 2017).

2463 In this study, i-pentane and n-pentane were highly correlated ( $R^2=0.87 - 0.94$ )  
2464 throughout the whole sampling campaign (Fig. 12), indicating constant pollution  
2465 sources for these two compounds. The highest ratio of i/n-pentane was found at JK  
2466 (2.59), which was comparable to the value of 2.93 reported in a Pearl River Tunnel  
2467 (Liu et al., 2008), thus indicating strong impacts from traffic-related sources. The  
2468 average ratio at MEM was 2.31, higher than the character ratios of coal combustion,  
2469 reasonably due to the observation site presented at upwind position of the thermal  
2470 power plant. Additionally, it is remarkable that MEM was surrounded by a main road  
2471 with four traffic lanes. The distance between the nearest traffic light and the sampling  
2472 site was just 200 m. Frequent idling may cover up the contribution from coal  
2473 combustion, reflecting the impact of traffic emissions. The average ratios at YH (1.94)  
2474 and GS (1.63) were lower than those at the above two sites, suggesting the  
2475 comparatively stronger contribution from coal burning.

2476 The T/B ratio is another efficient tool to differentiate pollution sources. Both the  
2477 tunnel and roadside researches indicated that T/B ratio varied within the range of 1 - 2  
2478 when the atmosphere was heavily impacted by vehicle emissions (Gentner et al.,  
2479 2013;Tang et al., 2007;Huang et al., 2015;Wang et al., 2002). The ratio of <0.6 was  
2480 ascribed to other sources such as coal combustion and biomass burning (Tsai et al.,  
2481 2003;Akagi et al., 2011). The industrial activity would be more dominant when the  
2482 T/B ratio is greater than 3 (Zhang et al., 2015).

2483 In this study, the correlation between benzene and toluene was fairly well at all  
2484 the sites ( $R^2=0.70-0.74$ ), except for YH ( $R^2=0.41$ ) (Fig.14), suggesting the similar  
2485 sources for benzene and toluene at JK, MEM and GS, while more complex such as  
2486 variable wind direction at YH. The average ratios of T/B were lied within the range of

2487 1.64-2.29, which were scattered around the character ratio of 2 for vehicle exhaust,  
2488 illustrating the significance of vehicle emissions at the four sites. Specifically, at JK,  
2489 MEM and YH, most of T/B ratios were distributed between 0.6 and 3, which were  
2490 corresponding to character ratios for coal or biomass burning and industrial activities  
2491 respectively. These reflected the mixture impacts from mobile source and  
2492 coal/biomass burning at these three sites. However, more values were greater than 3 at  
2493 GS, suggesting more frequent disturbance from industrial activities at this site.

2494 From the temporal respect, the T/B ratios at 14:00 LT were lower than at 07:00  
2495 LT (Fig.15). In fact, the reaction rate constant of toluene ( $5.63 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )  
2496 with  $\bullet\text{OH}$  is much higher than that for benzene ( $1.22 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ),  
2497 representing more rapid consumption of toluene from photochemical reactions and  
2498 thus resulting in lower T/B ratios at 14:00 LT. Besides, the emission strength of  
2499 mobile source is often weaker at 14:00 LT, while the coal/biomass burning are  
2500 increased due to more human activities. Both of the situations can be used to explain  
2501 the lower T/B ratios observed at 14:00 LT. In comparison with other months, higher  
2502 T/B ratios were found more frequently in September, potentially showing the more  
2503 strengthen industrial activities during this period.

2504 Overall, based on the iso-pentane/i-pentane and T/B ratios, the atmospheric  
2505 VOCs at every site were impacted by a mix of coal/biomass burning and vehicle  
2506 emissions, whereas GS was more liable impacted by industry-related sources.

### 2507 **3.6 Relative reactivity of VOCs**

2508 The reactivity of individual species was different, while mixtures of VOCs would  
2509 have competition the precursors between each other, leading to variations on reaction  
2510 paths and  $\text{O}_3$  formation yields. Ozone formation potential (OFP) is a useful tool to  
2511 estimate maximum  $\text{O}_3$  productions of each compound under optimum conditions,  
2512 from which the vital species in  $\text{O}_3$  formation could be identified (Huang et al., 2017).  
2513 The calculation of OFP is based on mixing ratios and maximum incremental reactivity  
2514 (MIR) of individual compound, which are expressed in Eq. (4).

$$2515 \text{OFP} = C_i \times \text{MIR} \quad (4)$$

2516 where  $C_i$  represents the concentration level of  $i^{\text{th}}$  species, while  $\text{MIR}$  is a constant

2517 taken from Carter (2010) (Table S1).

2518 In Zhengzhou city, alkenes contribute most ( $55.91 \pm 14.17\%$ ) to the sum of OFP,  
2519 of which ethylene had the largest portion. The results is different with the estimation  
2520 based on emission inventories by Wu and Xie (2017), in which the largest contributor  
2521 of total OFP in North China Plain (NCP), YRD and PRD was aromatics, reflecting  
2522 that there was relatively less surface coating industries in Zhengzhou.

2523 For the individual species, the top 10 most contributors in OFP included ethylene,  
2524 isoprene, m,p-xylene, toluene, propylene, acetylene, n-butane, i-pentane and propane.  
2525 Their contributions to the sum of OFP was lied within the range of 69.44 - 77.60%  
2526 (Table 5), with 61.30-76.46% of total VOCs weighted in concentration, highlighting  
2527 the importance of reduction on emissions of these VOCs no matter based on relative  
2528 reactivity or mixing ratios. Additionally, it is worth noting that, the percentage of  
2529 acetylene ( $4.51 \pm 0.34\%$ ) weighted in OFP was higher than many other areas in China,  
2530 including Guangzhou (2.20%) and YRD (2.37%) (Li and Wang, 2012;Jia et al., 2016),  
2531 demonstrating that it is necessary to conduct emission controls on sources related to  
2532 combustion (i.e., vehicle emissions and biofuel burning) in Zhengzhou city .

2533 Zhengzhou was suffered from the severest O<sub>3</sub> pollution in June, 2017. The  
2534 relationships between OFP of each organic group,  $\Sigma_{\text{VOCs}}$ , and the ambient  
2535 concentrations of NO<sub>x</sub> and O<sub>3</sub>, as well as the corresponding meteorological conditions,  
2536 are shown in Fig. S5-6. At 07:00 LT, generally lower WS was seen than that at 14:00  
2537 LT, offered a favorite condition for local O<sub>3</sub> propagation. Under low RHs and high T  
2538 and OFP ( $88.13 \pm 30.32$  ppbv), the O<sub>3</sub> level at YH was unexpectedly lower than that at  
2539 MEM on sunny days. Since the OFP was estimated with the assumption of reactions  
2540 that proceeded under optimum conditions, the above phenomenon reflected there  
2541 were unsatisfied O<sub>3</sub> formation conditions at YH. The highest total OFP was seen at JK  
2542 in June, while the highest O<sub>3</sub> levels was observed at GS where located at a downwind  
2543 position with lowest WS ( $0.74 \pm 0.33$  m s<sup>-1</sup>). The concentration level of O<sub>3</sub> usually  
2544 increased with wind speed (Fig.S7), particularly when the eastern wind was dominant,  
2545 illustrating the disturbance from long-distance sources to urban center.

### 2546 **3.7 Source apportionment**

2547 The factor profiles given by PMF for each site were presented in Fig.15. The six  
2548 factors were resolved as vehicle emissions, coal+biomass burning, solvent use, oil  
2549 evaporation, petrochemical and biogenic source (detailed characterization can be  
2550 referred to supporting information) on the base of the correspondent markers for each  
2551 source categories, which were summarized in Table S6. Meanwhile, the correlation  
2552 coefficients, expressed in Pearson's  $r$ , were varied from 0.54 to 0.62 and 0.66 to 0.73  
2553 for SO<sub>2</sub> with coal+biomass burning, and NO<sub>2</sub> with vehicle emission, respectively (Fig.  
2554 16), proved the precise results gained in this study.

2555 The weight percentage of each factor calculated with two criteria (absolute  
2556 concentrations and OFPs) at the four sites were presented in Fig.17. At every site,  
2557 vehicle emission, coal+biomass burning and solvent use were the top three  
2558 contributor to VOCs abundance in ambient air. Compared to JK and YH, even though  
2559 the distances between thermal power plant and the observation site was the shortest at  
2560 MEM, vehicle emission (36.82%) showed the largest portion instead. Coal+biomass  
2561 burning (30.58%) had the highest contribution at GS, attributed to its downwind  
2562 position and nearby suburbs that biomass burning occurred more frequently. The  
2563 contributions from vehicle emission at the two urban centers of MEM (36.82%) and  
2564 YH (37.39%) were comparable, but higher than those at JK and YH. The  
2565 consumptions of solvent at GS (18.86%) and JK (14.95%) were higher than those at  
2566 YH (10.1%) and MEM (11.48%), due to restriction on development of new industrial  
2567 enterprises in urban center in recent years. Emissions from oil evaporation,  
2568 petrochemical and biogenic emission were scarce, and their contributions were below  
2569 10% at every site.

2570 On the base of O<sub>3</sub> formation impact, coal+biomass burning, solvent use, and  
2571 vehicle emission were the three major contributors as well. In contrast to the  
2572 concentration weighted method, the importance of solvent use estimated with OFP  
2573 increased 28-65% for each site, and the significance of vehicle emissions decreased  
2574 29-53%. At YH and GS, small discrimination (<4%) in contributions of coal+biomass  
2575 burning between the two methods were found. On the other hand, the variations on  
2576 coal+biomass burning at JK (a decline of 17%) and MEM (an increase of 29%) were

2577 more obvious, due to low abundance of reactive species in this factor at JK and high  
2578 level of alkenes at MEM. Considering that the aging index of xylene/ethylbenzene  
2579 was high at MEM (2.97) and low at JK (0.01) remarkably, demonstrating that the  
2580 emission sources related to coal+biomass burning was fresher at MEM than JK.

2581 Except for oil gas evaporation and biogenic sources, in which major emitted  
2582 compounds with shorter life span, potential source regions for the other four identified  
2583 sources (i.e., coal+biomass burning, vehicle emission, solvent usage and  
2584 petrochemical) apportioned by PSCF method were presented in Fig. 18. Southwest of  
2585 Shanxi province, western of Shandong province, and southwest of Henan province  
2586 were identified as hot spots for the coal+biomass burning. The active emission areas  
2587 for solvent use were concentrated in Henan province, and mainly located in southwest  
2588 of Zhengzhou. The most contribution area for petrochemical was found in southwest  
2589 of both Shanxi and Henan, northwest of Anhui, and southeast of Hubei provinces. For  
2590 vehicle emissions, the strongest emission point was scattered in southwest of Henan,  
2591 while Shandong, Anhui and Hubei provinces also distributed with strong emission  
2592 points.

### 2593 **3.8 Consumption of VOCs and correlations with ozone level**

2594 The consumption of a VOC in the atmosphere could be presented as the  
2595 difference from its initial mixing ratio and the observed value. The groups of alkenes  
2596 and aromatics had larger consumption than alkanes, particularly at JK and GS  
2597 (Fig.19), which was consistent to stronger impacts from solvent usage at the two sites.

2598 The average value of VOC consumption at urban center (MEM and YH, 4-6ppbv)  
2599 was lower than that at marginal area (JK and GS, 9-11ppbv), and the average  
2600 increment of O<sub>3</sub> at 14:00 LT was higher than that at 07:00 LT in marginal area,  
2601 suggesting more efficient photochemical reactions at JK and GS. Meanwhile, the  
2602 average values of [•OH]Δt for each site, ranked in the same order with VOCs  
2603 consumption, were varied in a range of  $2.9 \times 10^{10}$  to  $4.71 \times 10^{10} \text{ cm}^{-3} \text{ s}$ . The values  
2604 were slightly lower than the results of  $4.9 \times 10^{10} \text{ cm}^{-3} \text{ s}$  measured at Beijing in  
2605 August-September, 2010 (Yuan et al., 2012), indicating that comparatively less aging  
2606 process in Zhengzhou.

2607 Taken the decrement of VOCs and NO<sub>x</sub> as independent variable and the  
2608 increment of O<sub>3</sub> as dependent variable, the multiple regression analysis was  
2609 performed. The results for JK and GS were presented as:

2610  $[O_3]_{\text{increment}}=0.41[VOC]_{\text{decrement}}+0.20[NO_x]_{\text{decrement}}+53.44$  (JK, R<sup>2</sup>=0.44)

2611  $[O_3]_{\text{increment}}=0.34[VOC]_{\text{decrement}}+0.39[NO_x]_{\text{decrement}}+59.29$  (GS, R<sup>2</sup>=0.38)

2612 The F values for JK and GS were 16.1 and 10.1 respectively, indicating the  
2613 regression results at the two sites were acceptable. However, the relationships among  
2614 O<sub>3</sub>, NO<sub>x</sub> and VOCs could not be expressed in this way at MEM and YH, where the  
2615 low values for both R<sup>2</sup> (0.12, 0.09) and F values (2.7, 2.8). This potentially attributed  
2616 to more constant disturbance from fresh emission sources at urban center.

#### 2617 **4. Conclusions**

2618 In this study, VOC samples were collected at four sites in Zhengzhou, Henan  
2619 (China) for the first time and analyzed for 57 species. It is found that the weighted  
2620 percentage of aromatics was lower, while alkyne was higher in Zhengzhou city than  
2621 in other Chinese cities. C2 - C5 alkanes, acetylene, ethylene, toluene and benzene  
2622 were the most abundant VOCs in the region, suggesting widespread  
2623 combustion-related sources in the city. On the basis of monthly average, the  
2624 maximum ΣVOCs was observed at GS site, where occasionally impacted from the  
2625 nearby gas fueled plant. Approximately 75% of VOCs/NO<sub>x</sub> ratios were below 6 at  
2626 each site, indicating that the O<sub>3</sub> formation was driven by VOCs regionally. Different  
2627 from other megacities, alkenes were the biggest contributors to OFP, and acetylene  
2628 was particularly critical at each site. In addition, the impact of aging process was less  
2629 in Zhengzhou than that in Beijing. The photochemical reactions at JK and GS were  
2630 more efficient, while the relationships among O<sub>3</sub>, NO<sub>x</sub> and VOCs at urban sites of  
2631 MEM and YH were more complex. Either the mixing ratios or calculated OFPs  
2632 demonstrated that the most important contributors to VOCs were vehicle exhaust,  
2633 coal+biomass burning and solvent use, illustrating the necessary to conduct emission  
2634 controls on these pollution sources. Vehicle emission was more dominant at urban  
2635 center (YH and MEM), while solvent use was more important at the sites (JK and GS)  
2636 far away from urban center in Zhengzhou. It is further shown that the air pollution in

2637 Zhengzhou was mostly impacted by local emissions according to the cluster analysis,  
2638 and southern air clusters occasionally from Hubei Province was cleaner. In addition,  
2639 strong emissions for coal+biomass burning were concentrated in southwest of Shanxi,  
2640 western of Shandong and southwest of Henan provinces according to the PSCF  
2641 analysis. Due to less anthropogenic emissions and more favorable dispersion  
2642 conditions, most of the air pollutants had the lowest levels in the mid-summer month  
2643 of July. This study provides the first-hand information on the characteristics of VOCs  
2644 and assists in overcoming the O<sub>3</sub> pollution issue in Zhengzhou city, China.

#### 2645 **Acknowledgements**

2646 This research was supported by the Key Program of National Natural Science  
2647 Foundation of China (Grant No. 91744209).

2648 **Table & Figure**

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Table1. Concentrations of  $\Sigma_{\text{VOCs}}$  (ppbv) at every site during the sampling period

	<b>JK</b>		<b>MEM</b>		<b>GS</b>		<b>YH</b>	
	<b>Mean</b>	<b>Std.</b>	<b>Mean</b>	<b>Std.</b>	<b>Mean</b>	<b>Std.</b>	<b>Mean</b>	<b>Std.</b>
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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Table2. Wind speed ( $\text{m}\cdot\text{s}^{-1}$ ) at every site during the sampling period

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

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2655 Table3. Concentration levels of VOCs and compositions of major groups in Zhengzhou and other  
 2656 cities in China

Items	Guangzhou	Nanjing	Beijing	Hangzhou	Wuhan	Zhengzhou
	March-December, 2005	2011-2012	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
Compositions of major groups (%)	<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., 2017b)	(Lyu et al., 2016)	this study

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Table4. Specific information on VOCs, O<sub>3</sub> 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
Σ <sub>VOCs</sub> (ppbv)	34.02	30.28	28.33	39.29
O <sub>3</sub> (ppbv)	74.87	73.50	73.81	87.99
NO(ppbv)	7.10	7.72	2.34	4.47

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2661 Table5. Top 10 VOCs ranked according to calculated ozone formation potential (OFP) and their

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corresponding percentage weighted in mixing ratio

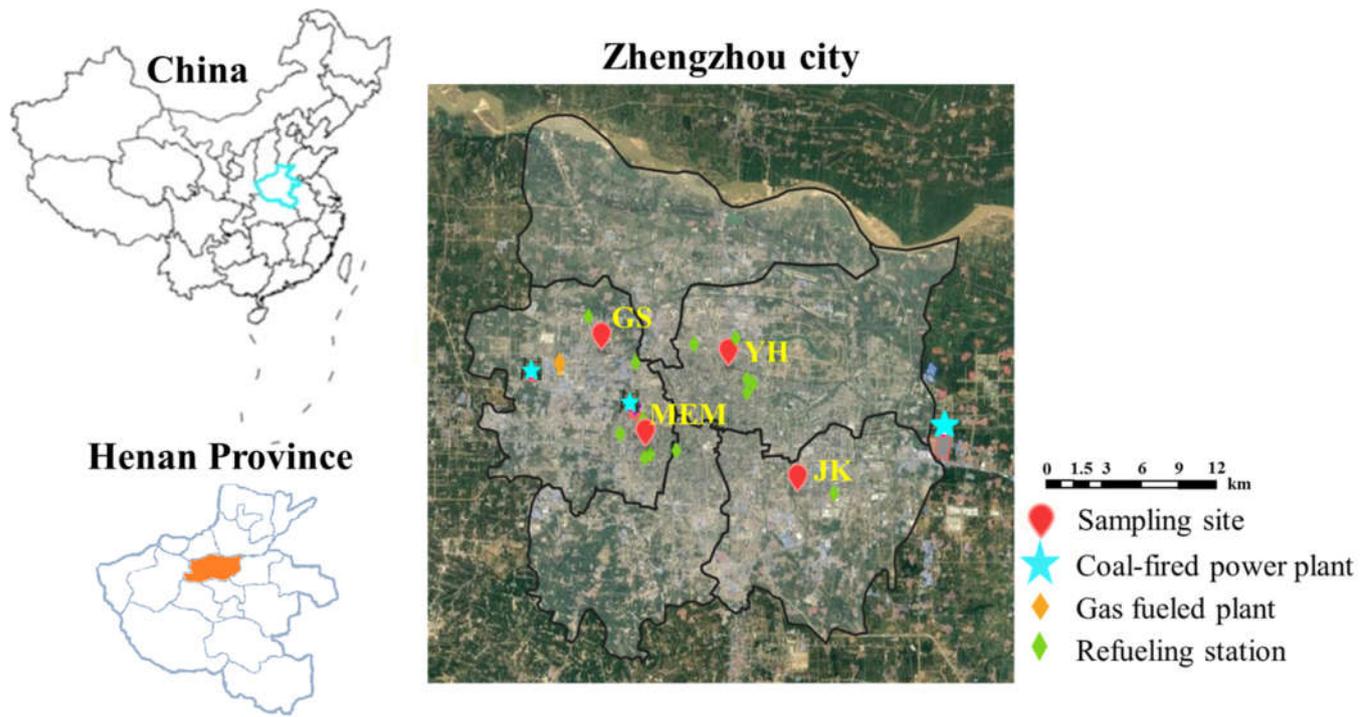
Site	Species	OFP (ppbv)	Weighted in OFP (%)	Weighted in mixing ratio (%)	Site	Species	OFP (ppbv)	Weighted in OFP (%)	Weighted in mixing ratio (%)
JK	Ethylene	18.99	25.54	8.22	MEM	Ethylene	18.44	30.88	7.92
	Isoprene	12.99	21.83	7.31		Isoprene	4.66	10.10	2.36
	m/p-Xylene	6.08	5.89	2.67		Toluene	3.73	6.67	3.99
	Toluene	5.53	5.83	4.22		Propylene	3.60	6.16	1.25
	Propylene	4.03	5.36	1.29		Acetylene	2.82	5.00	12.19
	Acetylene	2.97	4.44	13.54		m/p-Xylene	2.55	4.20	1.40
	n-Butane	2.15	3.05	7.28		n-Butane	1.81	3.20	5.97
	o-Xylene	1.83	2.00	0.88		Isopentane	1.76	3.16	7.39
	Isopentane	1.66	1.95	6.50		Ethane	1.58	2.96	23.35
	Propane	1.17	1.73	9.77		Propane	1.31	2.48	10.64
YH	Ethylene	19.83	28.10	8.88	GS	Ethylene	18.04	25.96	7.51
	Isoprene	7.44	11.30	3.67		Isoprene	8.01	16.75	4.64
	Toluene	6.63	7.75	5.72		Toluene	7.43	7.67	5.49
	m/p-Xylene	3.93	4.38	1.58		Propylene	4.39	5.85	1.26
	Acetylene	3.15	4.38	13.91		m/p-Xylene	4.31	4.57	1.75
	Propylene	3.01	3.60	0.91		Acetylene	2.76	4.24	12.07
	Trans-2-pentene	2.25	2.94	3.43		n-Butane	1.82	2.93	6.39
	n-Butane	1.84	2.80	6.31		Isopentane	1.71	2.68	6.94
	Isopentane	1.59	2.22	6.69		Propane	1.38	2.26	11.61
	Propane	1.18	1.98	10.20		Isobutane	1.13	1.98	4.59

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<sup>a</sup> *m*-Xylene and *p*-Xylene are co-eluted in the chromatographic separation.

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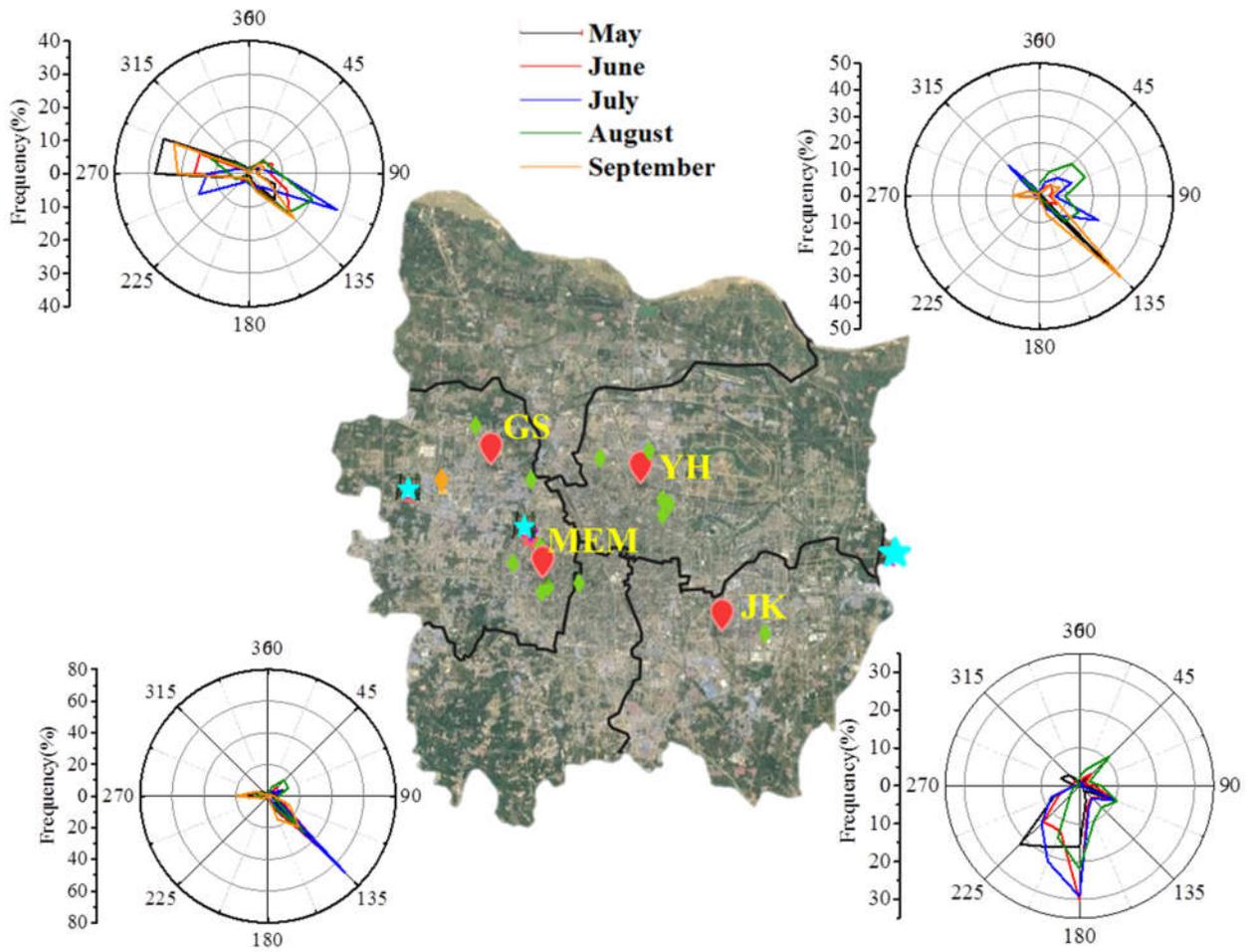


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Fig 1. Map of Zhengzhou, China showing the locations of sampling sites.

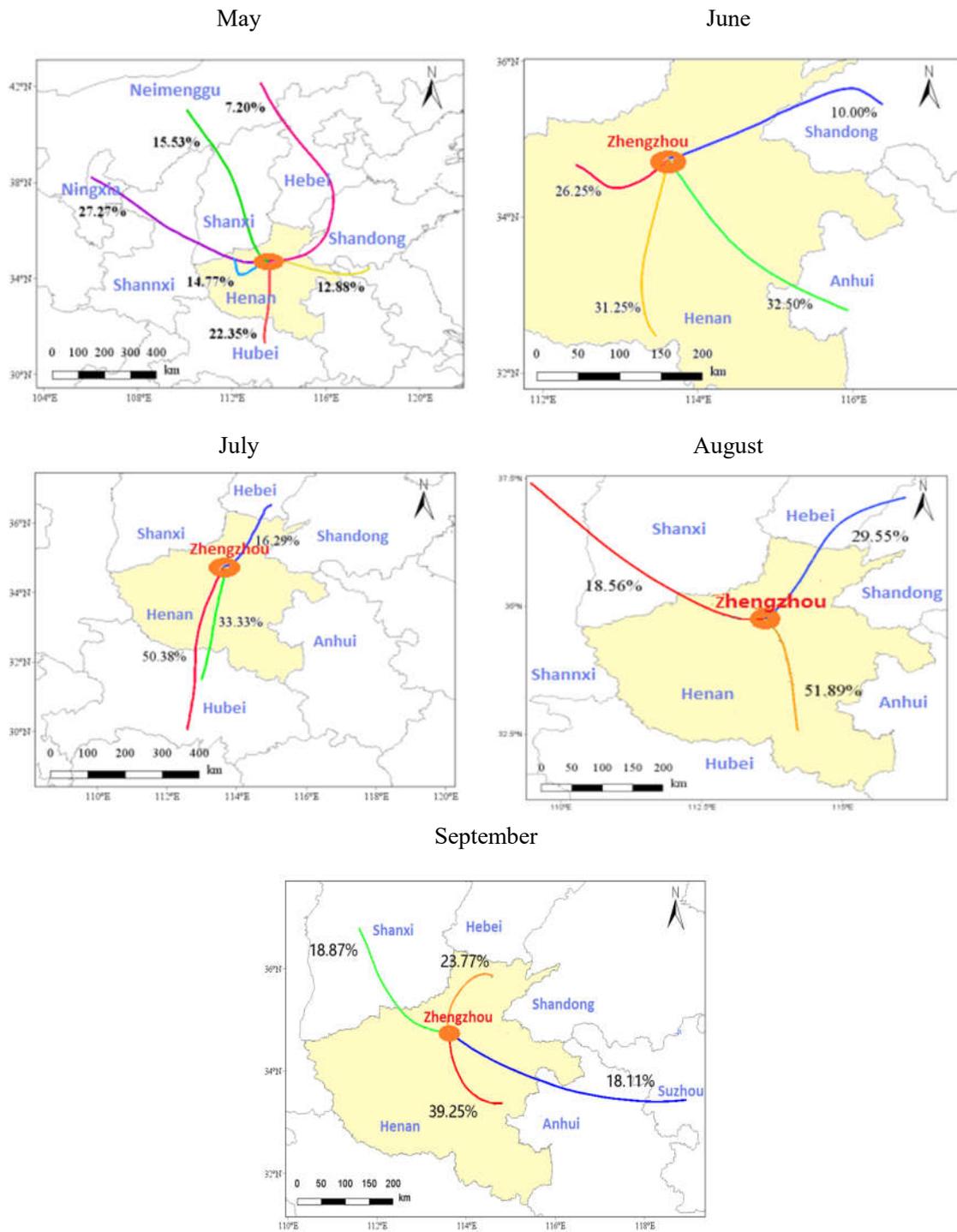


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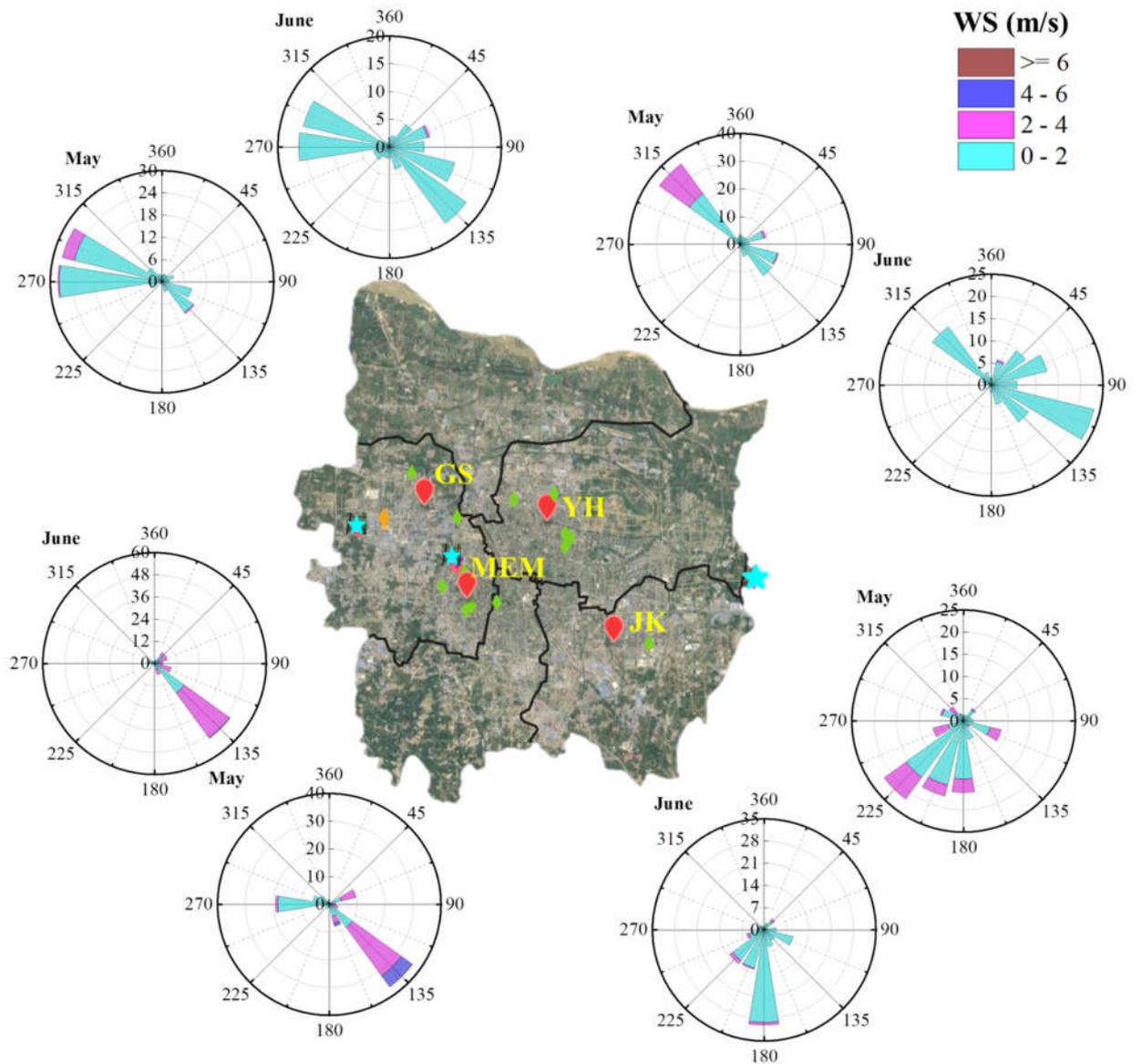
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Fig.2 Wind direction for each site during May to September, 2017



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Fig. 3 Cluster analysis of Zhengzhou in each sampling month



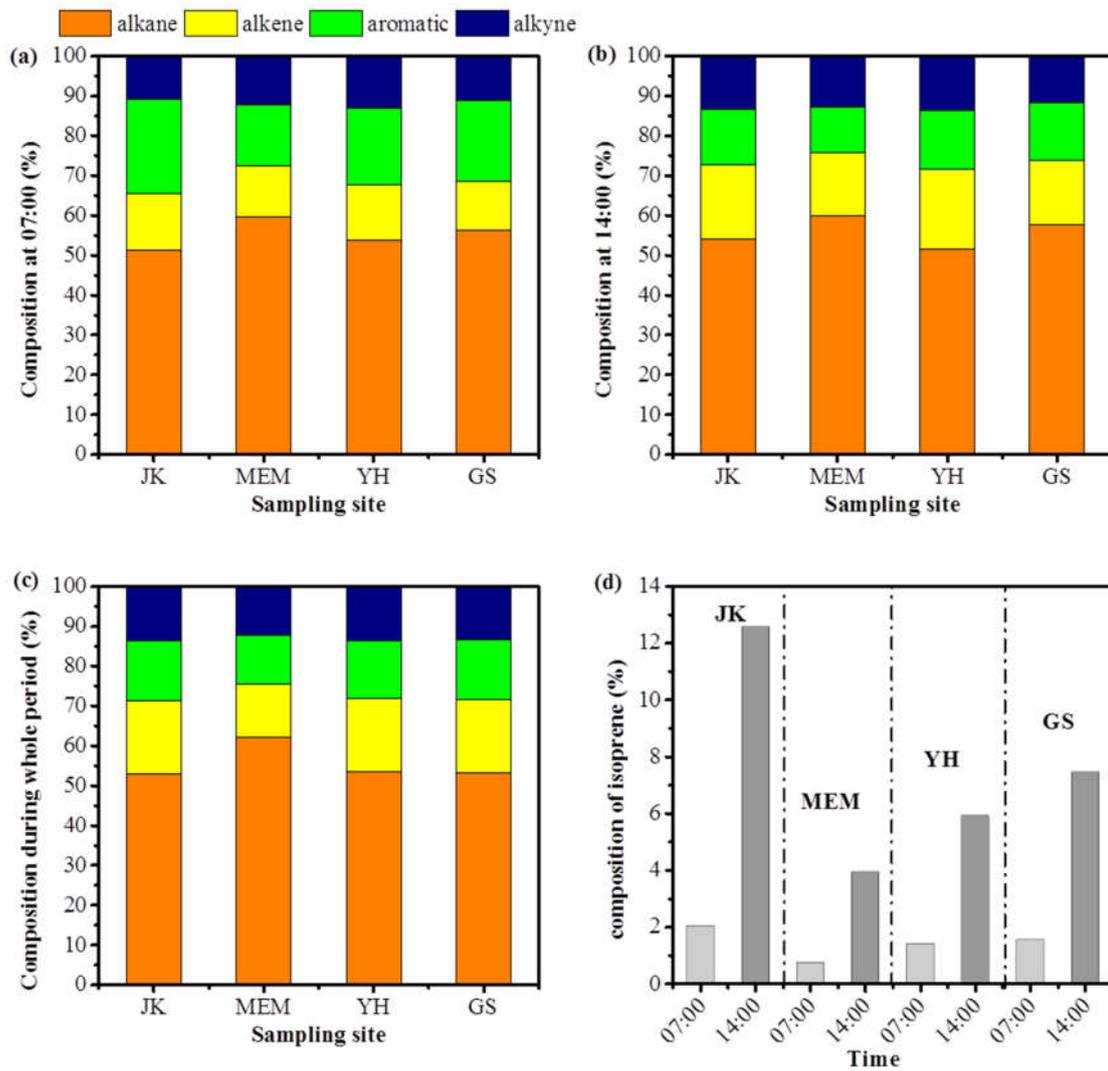
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Fig.4 Wind rose at each site in May and June (the wind distribution in other three months were illustrated in Fig S2)

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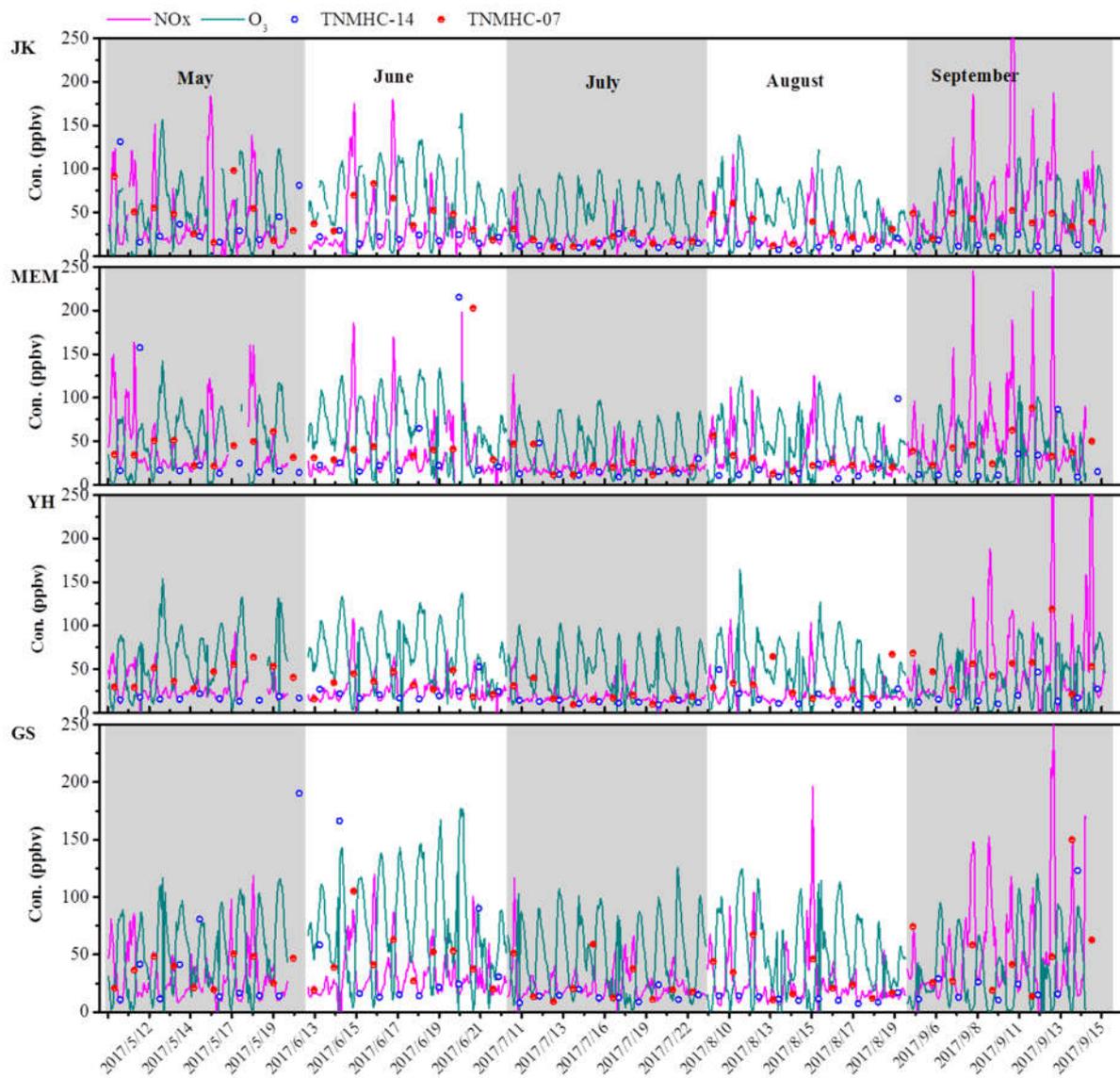
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2679 Fig. 5 Compositions of major organic classes at 07:00 LT (a), 14:00 LT (b) and during the whole  
 2680 sampling period (c) at the four sites, and the composition of isoprene at 07:00 LT and 14:00 LT for  
 2681 each site (d).

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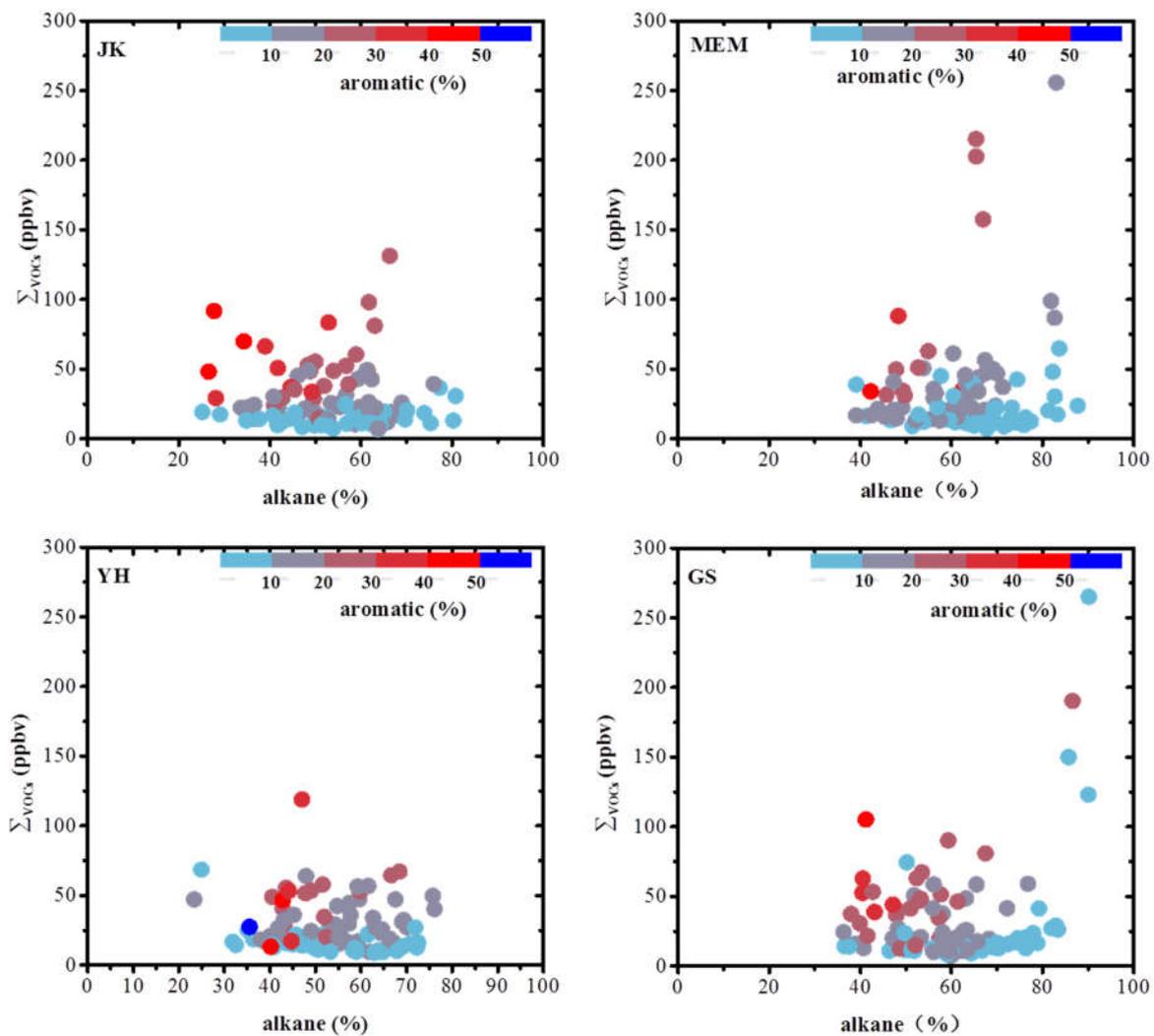


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2684 Fig.6 Temporal variations of mixing ratios of  $\Sigma_{\text{VOCs}}$ , NO<sub>x</sub> and O<sub>3</sub> at the four sites during the whole  
 2685 sampling period, in which  $\Sigma_{\text{VOCs-07}}$  stands for the concentration level of  $\Sigma_{\text{VOCs}}$  observed at 07:00  
 2686 LT, and  $\Sigma_{\text{VOCs-14}}$  was that observed at 14:00 LT.

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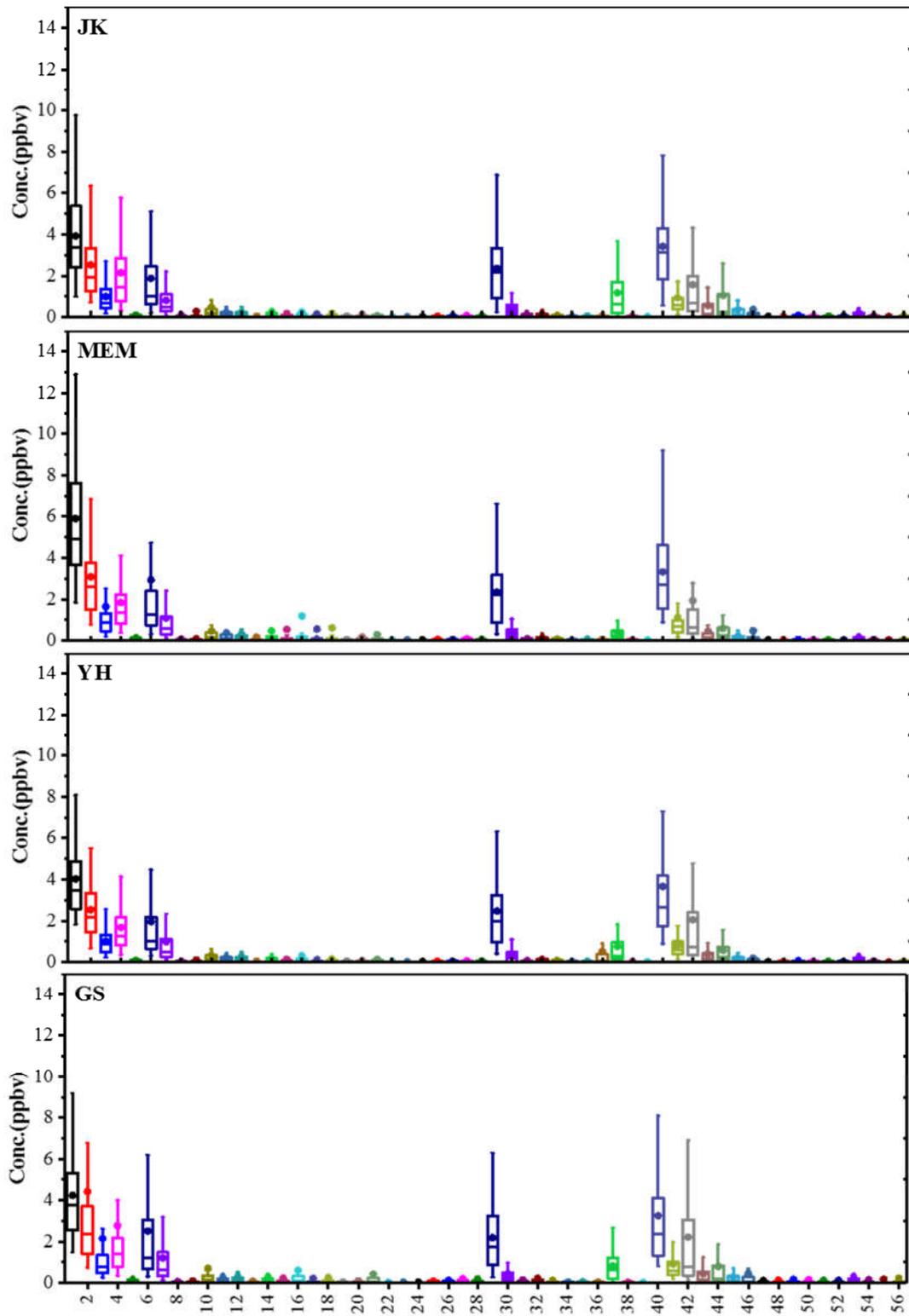
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Fig. 7 The relationship between mixing ratio of  $\Sigma_{VOCs}$  and the composition of alkane, the data points were color coded with the composition of aromatic.



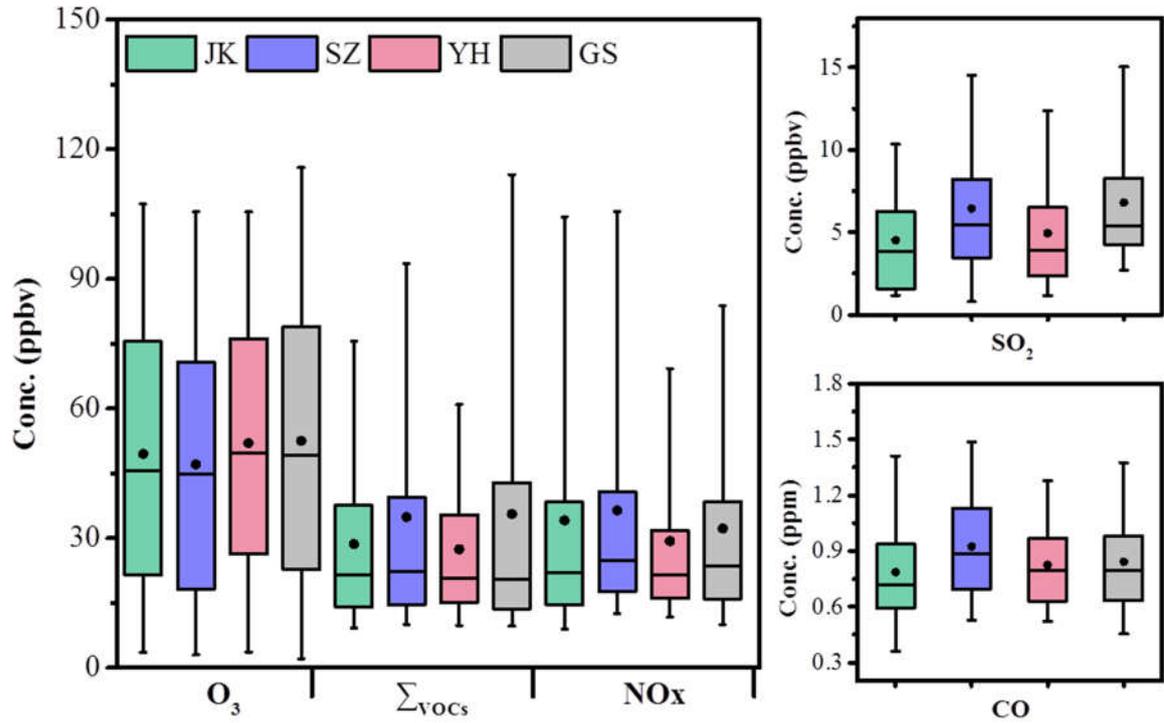
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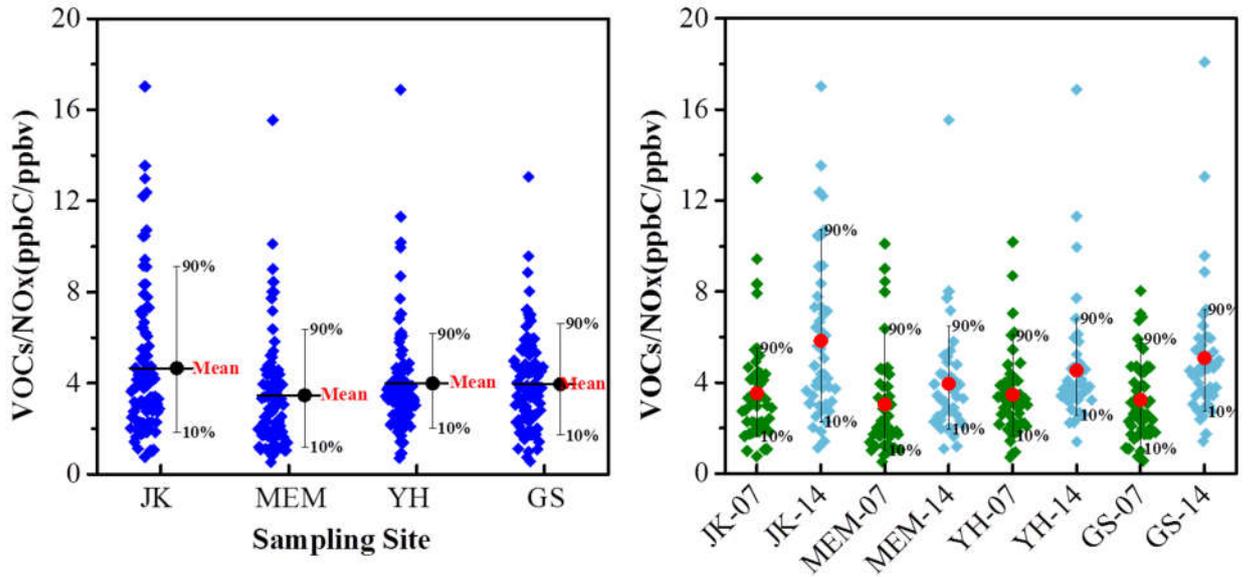
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Fig.8 Concentrations of 57 VOCs at each site for the whole sampling period, the whisker was ranged from 5-95%, and the box was 25-75%, the solid points stand for average value, the line in the box represent median value. The number of chemicals can refer from Table S1.



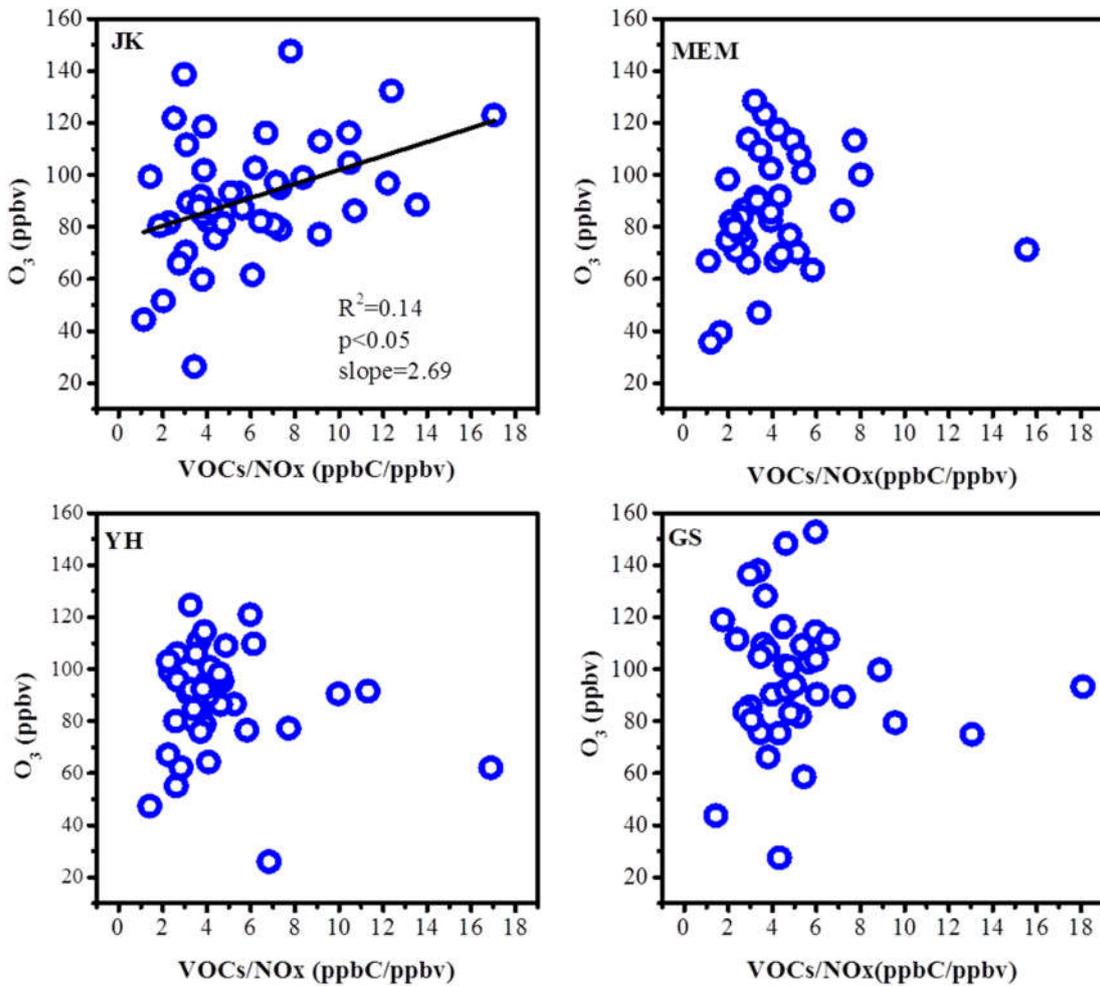
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Fig. 9 The distribution of concentration point on O<sub>3</sub>, ΣVOCs, NO<sub>x</sub>, SO<sub>2</sub> and CO at each site, the range of the box was 25%-75%, the black line in the box stands for median level, the black dot represent the average level, the range of whisker was 5-95%.



2702  
 2703  
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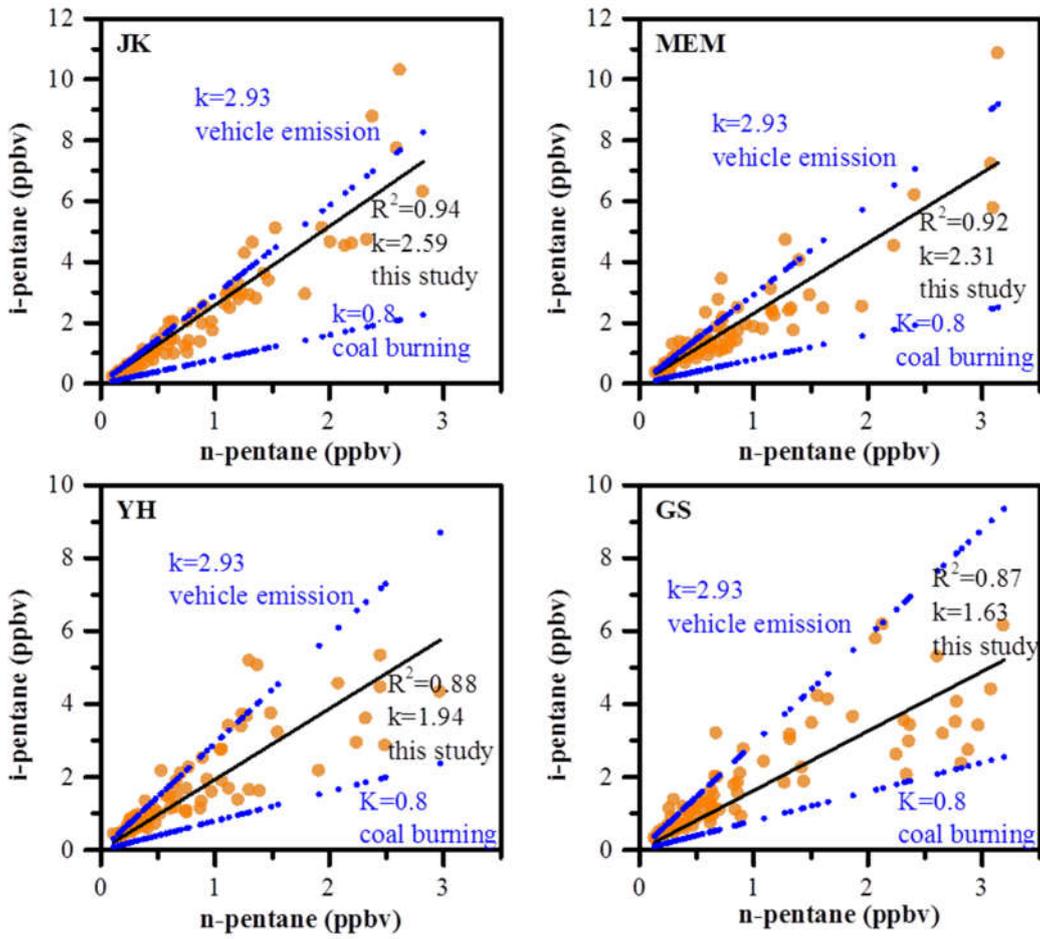
Fig.10 The data distribution of VOCs/NO<sub>x</sub>(ppbC/ppbv) at the four sites (left), and the ratio observed at 07:00 LT and 14:00 LT were presented (right).



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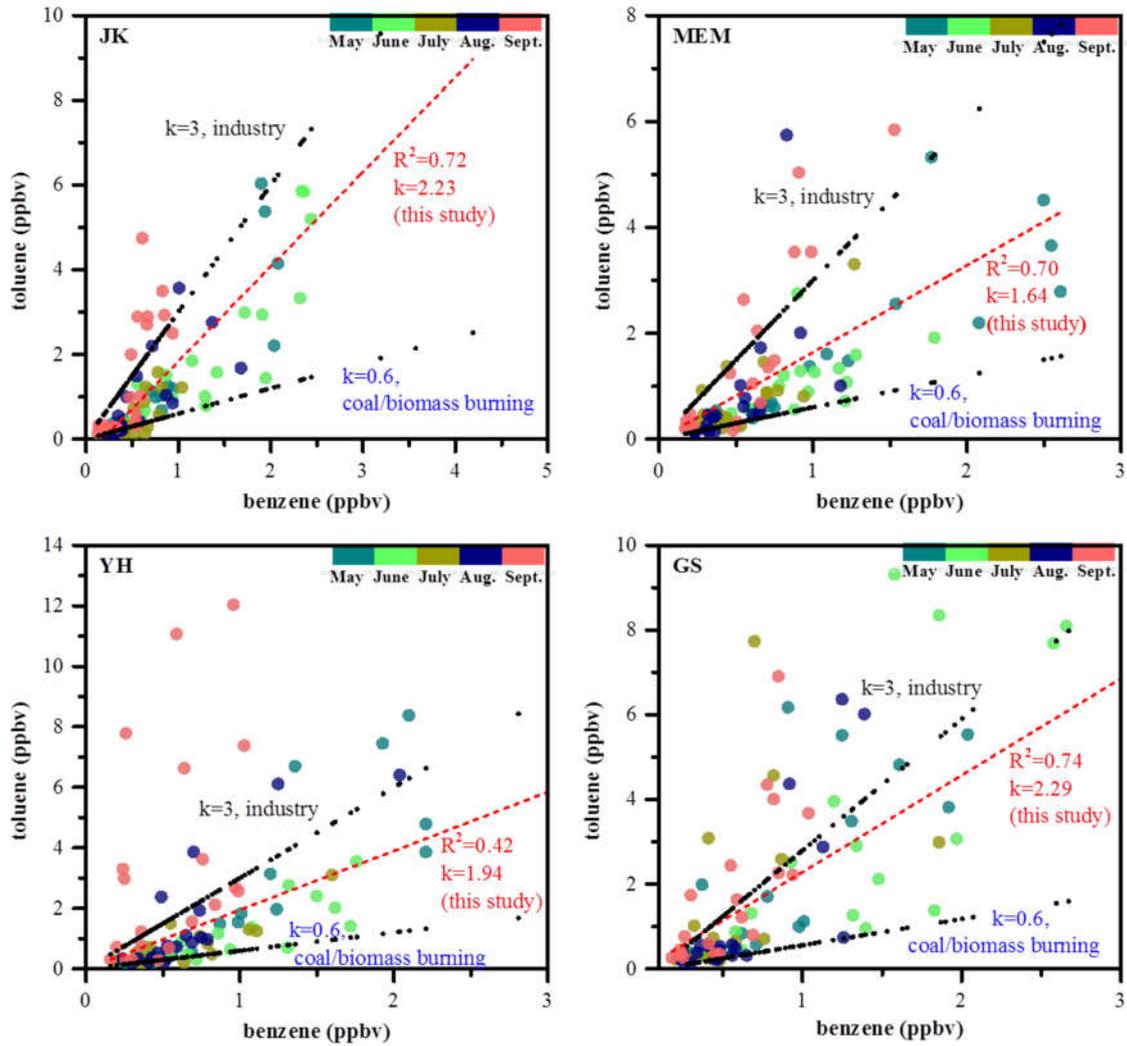
Fig.11 The relationship between O<sub>3</sub> and VOCs/NO<sub>x</sub> at 14:00 LT

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Fig. 12 Ratios of isopentane to n-pentane at every site



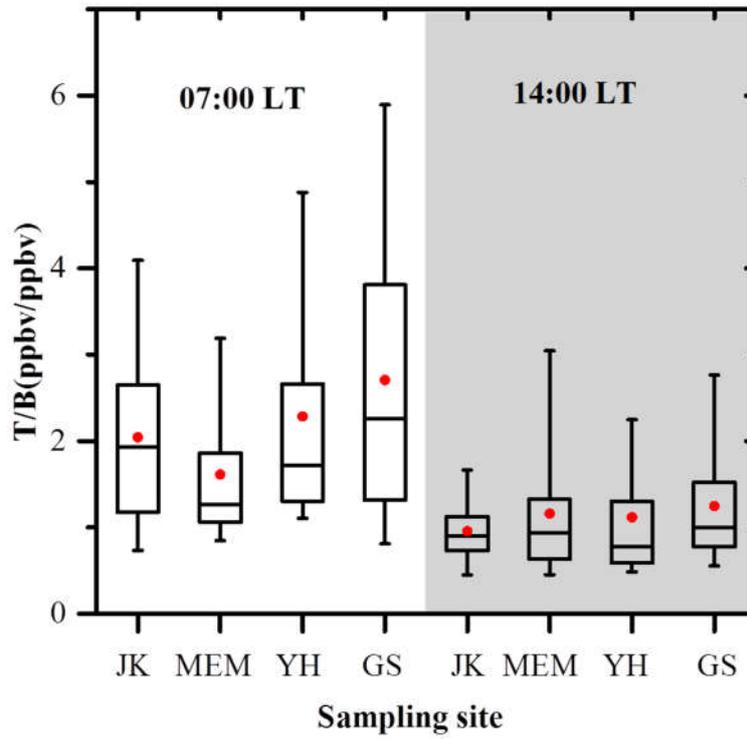
2714

2715 Fig.13 T/B ratios and linear correlation coefficients ( $R^2$ ) between benzene and toluene at every site,  
 2716 the data points were color mapped with sampling period.

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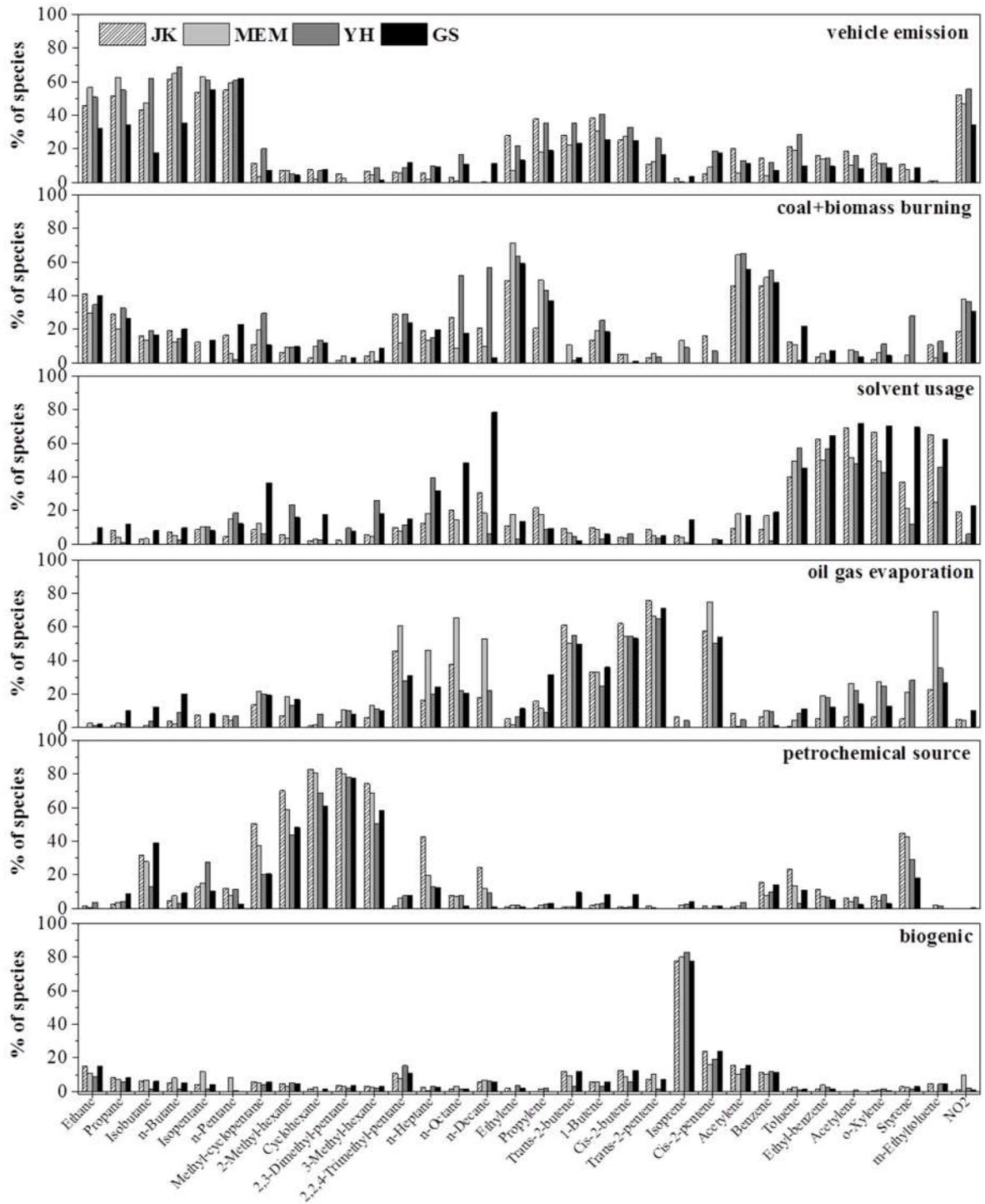
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2721 Fig. 14 The average ratio of T/B at 07:00LT and 14:00LT for each site during the whole sampling  
2722 period

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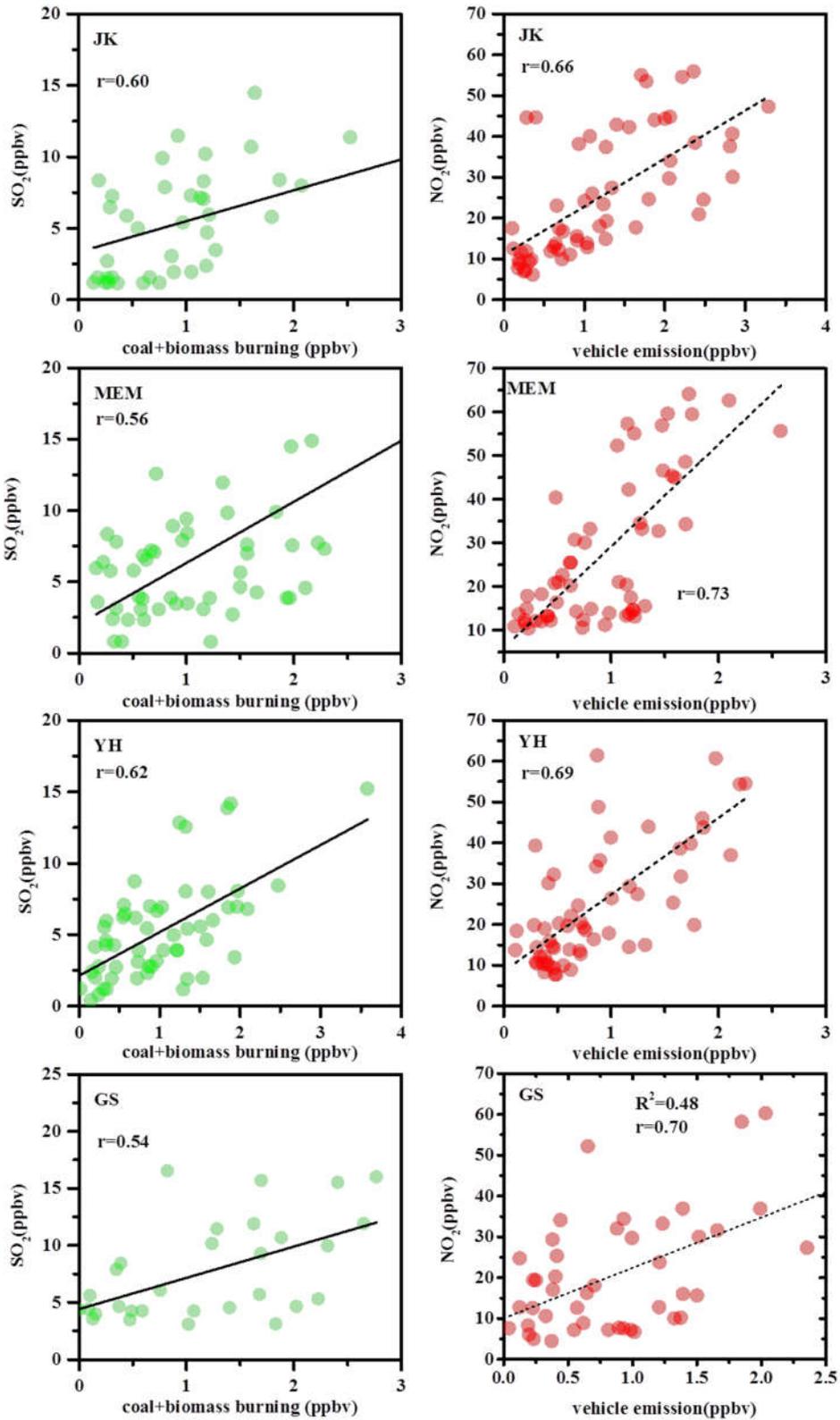
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Fig. 15 Explained variations in source profiles as identified by PMF

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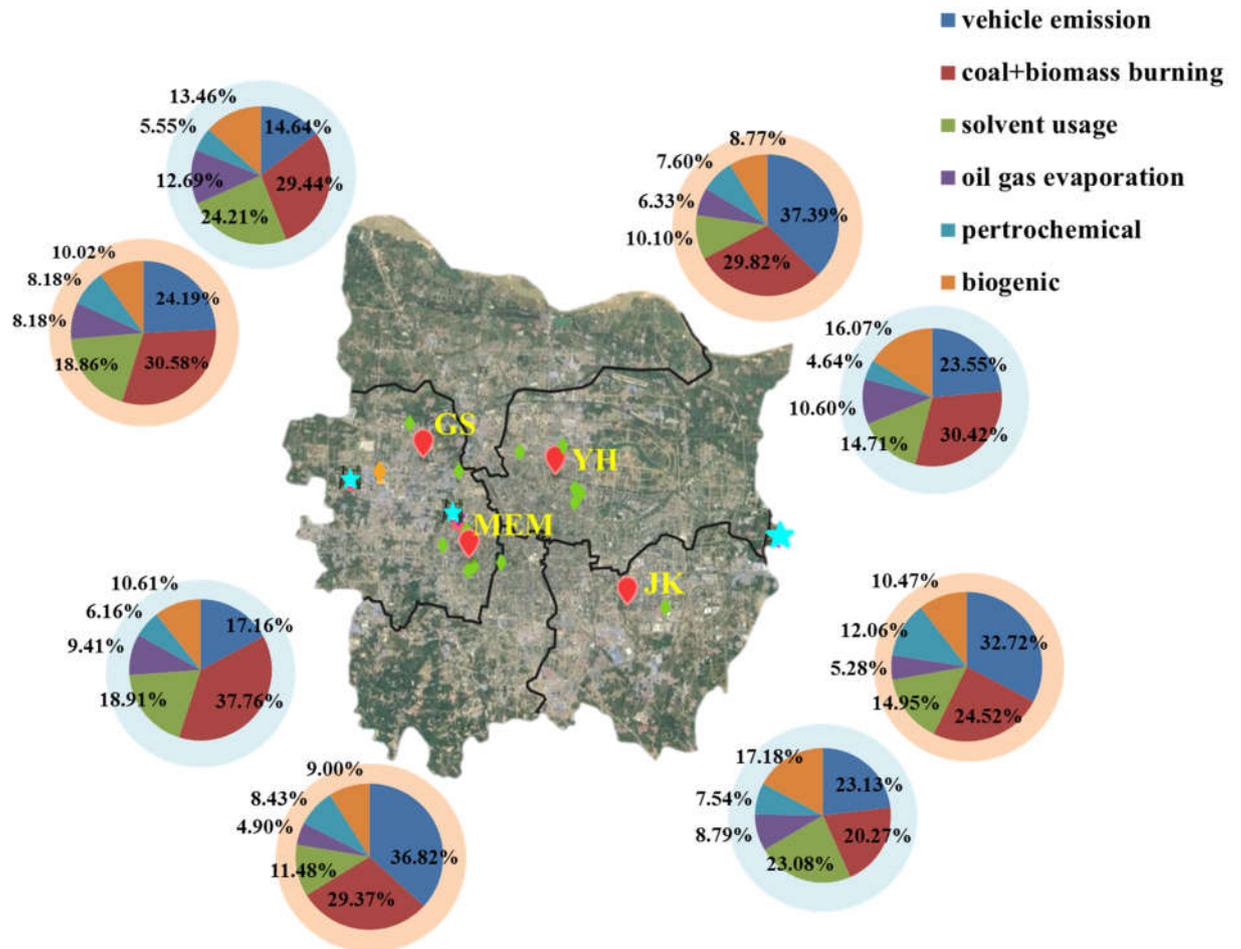
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Fig. 16 Correlation analysis between contributions of coal+biomass burning and SO<sub>2</sub>, and vehicle emission and NO<sub>2</sub>



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Fig. 17 Source apportionment results during the whole sampling period. The results weighted in observed concentrations were shadowed with pink color, and the results estimated based on OFP were shadowed with light blue color.

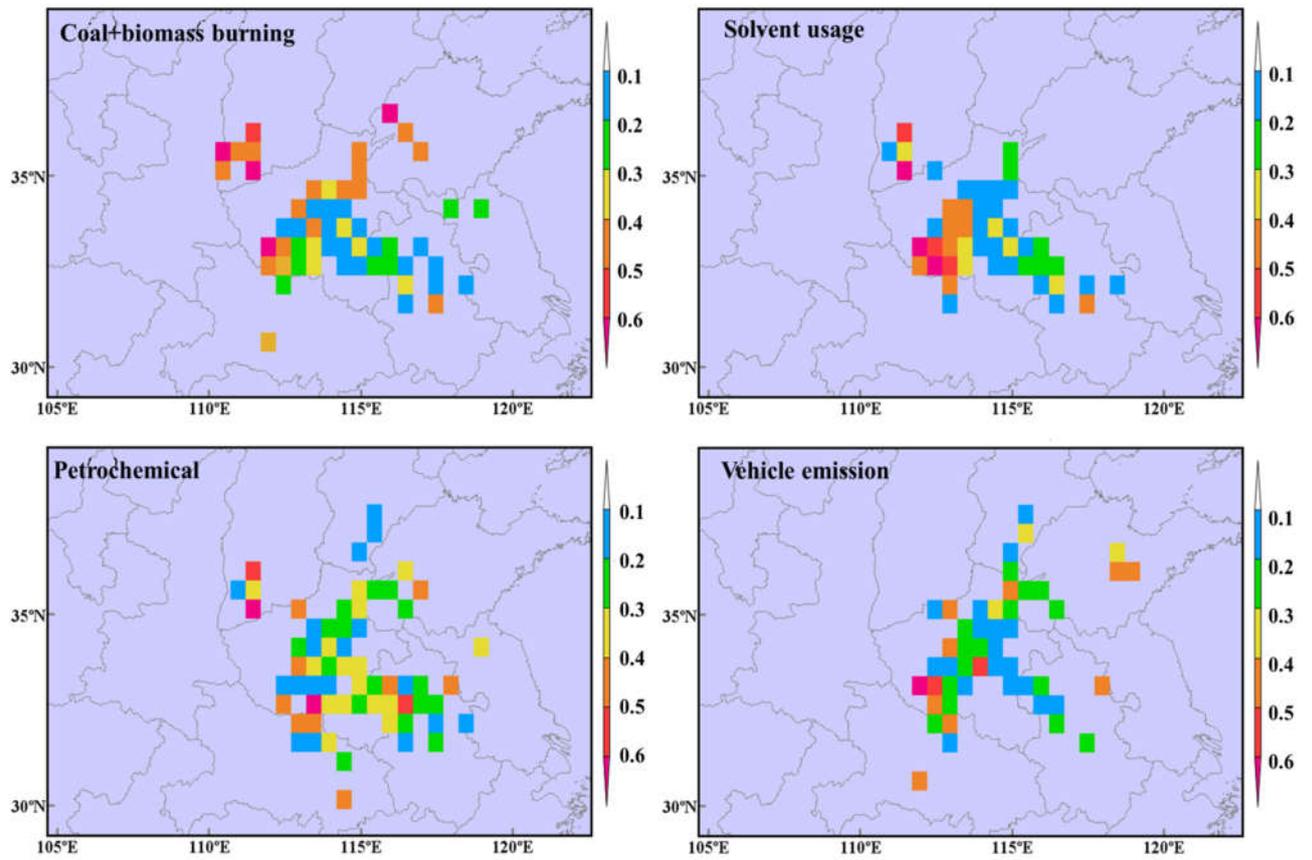
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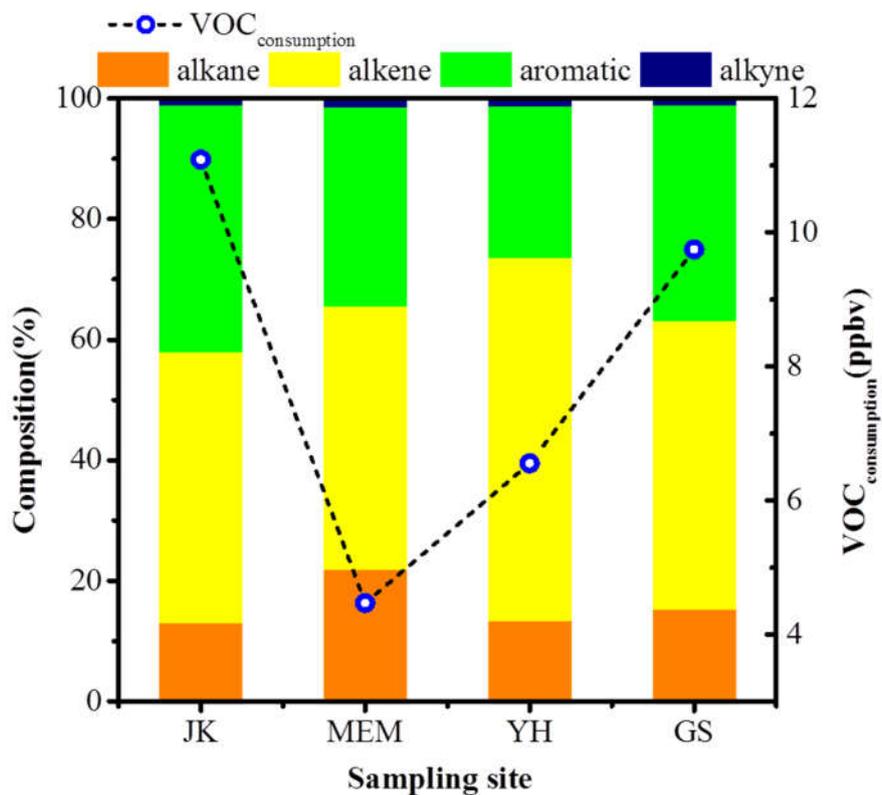
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2741 Fig. 18 Probable source regions apportioned by PSCF at Zhengzhou at summer (June-Aug. 2017)  
2742 during sampling period

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Fig. 19 The composition of major groups based on chemical consumption and the total consumption at each site.

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