Volatile organic compounds at a rural site in Beijing: Influence of temporary emission control and wintertime heating

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32 **Abstract**

33   Secondary organic aerosols (SOA) contribute substantially to $PM_{2.5}$ during

34 wintertime severe haze events in north China, yet ambient volatile organic compounds

35 (VOCs) as SOA precursors are comparatively much less characterized in winter

36 especially in rural areas. In this study, ambient air samples were collected in 2014

37 from 25 October to 31 December at a rural site inside the campus of University of

38 Chinese Academy of Sciences (UCAS) in northeast Beijing for the analysis of VOCs.

39 Since that temporary intervention measures were implemented during 3-12 November

40 to improve air quality for the Asian-Pacific Economic Cooperation (APEC) summit

41 held in 5-11 November in Beijing, and that wintertime central heating started since 15

42 November in Beijing after the APEC summit, it is a good opportunity to study the

43 influence of the temporary control measures and the wintertime heating on the

44 ambient VOCs. As a result of temporary intervention measures implemented during

45 3-12 November (period II), total mixing ratios of non-methane hydrocarbons averaged

46 11.25 ppb, about 50% lower than that of 23.41 ppb before the APEC (25 October-2

47 November; Period I) or 21.71 ppb after the APEC (13 November-31 December;

48 Period III). Their ozone and SOA formation potentials decreased by ~50% and ~70%,

49 respectively, with the larger drop in SOA formation potentials attributed to more

50 effective control of aromatic hydrocarbons mainly from solvent use. Back trajectory

51 analysis revealed that the average mixing ratios of VOCs in the southerly air masses

52 were 2.3, 2.3 and 2.9 times that in the northerly ones during period I, II and III,

53 respectively; and all VOC episodes occurred under the influence of southerly winds,

54 suggesting much stronger emissions in the south urbanized regions than in the

55   northern rural areas. Based on the positive matrix factorization (PMF) receptor model,

56   changed contributions from traffic emission and solvent use could explain 47.9% and

57   37.6% of the reduction in ambient VOCs, respectively, during the Period II relative to

58   the Period I, indicating that the temporary control measures on vehicle emission and

59   solvent use were effective in lowering ambient levels of VOCs. Coal/biomass burning,

60   gasoline exhaust, and industrial emission were among the vital sources, and they

61   altogether contributed 60.3%, 78.6% and 78.7% of VOCs during the period I, II and

62   III, respectively. Coal/biomass burning, mostly residential coal burning, became the

63   dominant source which accounted for 45.1% of the VOCs during the wintertime

64   heating period, with a remarkably lower average contribution percentage (38.2%) in

65   the southerly air masses than that of 48.8% in the northerly air masses.

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1. Introduction

67

68   Volatile organic compounds (VOCs) are precursors of tropospheric ozone and

69 secondary organic aerosols (SOA) (Forstner et al., 1997; Odum et al., 1997; Atkinson,

70 2000; O'Dowd et al., 2002; Sato et al., 2010). As SOA are important components of

71 $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) (Cabada et

72 al., 2004; Lonati et al., 2005; Huang et al., 2014), reducing emission of VOCs would

73 benefit improving air quality in megacities, such as China's capital city Beijing,

74 where air pollution has become an extensive concern with increasing surface ozone

75 levels during summertime and severe $PM_{2.5}$ pollution during wintertime (Streets et al.,

76 2007; Ji et al., 2012; Wang et al., 2014). Since higher levels of ozone mostly occur

77 during summer and ozone formation in urban areas is largely VOC-limited (Shao et

78 al., 2009; Tang et al., 2010), many field measurements of VOCs in Beijing were

79 conducted in summertime with a focus on their sources (Song et al., 2007; Lu et al.,

80 2007; Yuan et al., 2009; Wang et al., 2010a) and their mixing ratios as well,

81 particularly during ozone episodes (Liu et al., 2009; An et al., 2012; Zhang et al.,

82 2012a; Liu et al., 2013). However, comparatively the role of VOCs in the wintertime

83 with $PM_{2.5}$ pollution is much less understood.

84   During extremely severe and persistent haze events in China, organic matter

85 (OM) could contribute 30-70% of the total $PM_{2.5}$, and higher fractions of SOA in OA

86 were observed during polluted days in winter in Beijing (Guo et al., 2014; Huang et

87 al., 2014; Zhang et al., 2014a). Therefore, the control of VOCs, as SOA precursors, is

88 also of great importance in the control of air pollution by $PM_{2.5}$ in wintertime. A

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89 previous study demonstrated that levels of aromatic hydrocarbons and carbonyls

90 increased significantly under haze days in urban Beijing from 2008 to 2010 (Zhang et

91 al., 2014b), yet few reports are available about wintertime precursor VOCs in Beijing.

92 In urban areas, vehicle exhausts are important sources of SOA precursors (McDonald

93 et al., 2015; Liu et al., 2015a; Ortega et al., 2016; Deng et al., 2017; Gentner et al.,

94 2017). However, biomass/biofuel burning and coal burning may also contribute

95 substantially to SOA precursors (Yokelson et al., 2008; Shrivastava et al., 2015; Fang

96 et al., 2017), particularly in north China in wintertime when raw coal and biofuels are

97 widely used for household heating (Liu et al., 2016; Zhang et al., 2016a; Liu et al.,

98 2017). In fact, a study by Wang et al. (2013) in 2011-2012 revealed that even at an

99 urban site in Beijing coal combustion could account for 28-39% of VOCs observed in

100 ambient air. As raw coal and/or biofuel burning is widely occurring in the rural areas

101 in wintertime (Liu et al., 2016), it is necessary to investigate how the enhanced

102 emission due to wintertime household heating would influence the levels and

103 compositions of VOCs in rural areas, as forming SOA or ozone is an issue of regional

104 scale.

105   Due to a wide variety of emission sources of VOCs and large uncertainties of the

106 emission inventories of VOCs, to assess the effect of emission control measures on

107 reducing ambient VOCs is a highly challengeable task. The Chinese government has

108 implemented long-term pollution control actions and air quality has been greatly

109 improved in north China in recent years (Hao and Wang, 2005; Wang et al., 2009;

110 Zhang et al., 2012b; Liu et al., 2015b; Kelly and Zhu, 2016). However, air quality in

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111   Beijing is not so satisfactory when compared to that in cities in the United States and

112   Europe, especially in wintertime with frequent haze events and high $PM_{2.5}$ levels.

113   Consequently, during critical international events such as the 2008 Olympic Games

114   (Wang et al., 2010b; Huang et al., 2010) and the 2014 Asia-Pacific Economic

115   Cooperation (APEC) summit, temporary intervention measures were adopted to

116   guarantee better air quality. This kind of temporary intervention provided a good

117   opportunity to study the effectiveness of various control measures on the reduction of

118   ambient air pollutants including VOCs (Yao et al., 2013; Huang et al., 2017). As for

119   the 21th Asia-Pacific Economic Cooperation (APEC) summit held in Beijing on 5-11

120   November 2014, temporary control measures in Beijing and its surrounding regions

121   resulted in significant drops of air pollutants including $PM_{2.5}$ and NOx (Huang et al.,

122   2015; Liu et al., 2015c; Wang et al., 2015; Xu et al., 2015; Zhang et al., 2016b); For

123   the VOCs in ambient air, as observed by Li et al. (2015) at an urban site inside the

124   campus of Peking University, total mixing ratios of VOCs reduced by 44% during the

125   APEC summit control period when compared to the period before. Since most

126   observation-based evaluations about the effectiveness of temporary emission control

127   measures were made with monitoring data in the urban areas, it is entirely necessary

128   to further investigate the influence in rural areas or a regional scale.

129   In this study, ambient air samples were collected at a rural site in the north of

130   Beijing from 25 October to 31 December 2014, covering the period with the enhanced

131   temporary emission control (3-12 November) for the APEC summit and the

132   wintertime heating period starting from 15 November. The objectives of present study

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133 are: (1) to study changes in the mixing ratios and compositions of VOCs at a rural site

134 in Beijing in response to the emission control during the APEC summit and the

135 wintertime heating; (2) to identify crucial sources of VOCs in Beijing and their

136 changes during the PM-polluted wintertime; (3) to evaluate the impact of control

137 measures implemented during APEC summit on the reduction of VOCs in ambient air

138 in rural areas.

139 **2. Methodology**

140 *2.1 Sampling Site and Field Sampling*

141   The ambient air samples were collected at a site (40.41° N, 116.68° E; Fig. 1)

142 inside the campus of University of Chinese Academy of Science (UCAS) in Huairou

143 district of Beijing. The UCAS is located about 60 km northeast of central Beijing and

144 about 150 km northwest of the Tianjin city. It is surrounded by several small villages

145 and farmlands. The samples were collected 16 meters above ground on the top of a

146 four-story building, about 100 m west of a national road and only 1.5 km far away

147 from the APEC main conference hall.

148   Ambient air samples were collected from 25 October-31 December 2014 using

149 cleaned and evacuated 2 L silica-lined stainless steel canisters. During field sampling,

150 a model 910 canister sampler (Xonteck Inc., California, USA) with a constant flow

151 rate of 66.7 ml min^{-1} was adopted to allow each canister to be filled in 60 min.

152 Samples were collected at approximately 10:00 and 15:00 of local time (LT) on sunny

153 days, one or two more samples were collected at 12:00 and/or 18:00 LT on haze days

154 when the visibility less than 10 km at relative humidity less than 90% (Fu et al., 2016).

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155 A total of 153 samples were collected during sampling. According to the air pollution

156 control measures, the field campaign was divided into periods I (25 October-2

157 November), II (3-12 November) and III (13 November-31 December). Period II was

158 the   time   span   when   temporary   control   measures   (Table   1;

159 http://www.zhb.gov.cn/gkml/hbb/qt   /201411/t20141115_291482.htm)   implemented

160 for better air quality. Wintertime heating started on 15 November just after the cease

161 of temporary control measures on 13 November. During the sampling periods,

162 prevailing winds were mostly from north to northwest (315-360°), the average wind

163 speeds were 3.5, 3.9, and 4.1 m s^{-1}, and average temperature was 11.4, 7.0, and 0.6°C

164 during periods I, II and III, respectively.

165 *2.2 Laboratory Analysis of VOCs and Carbon Monoxide*

166   All ambient air samples were analyzed with a Model 7100 pre-concentrator

167 (Entech Instruments Inc., California, USA) coupled with an Agilent 5973N gas

168 chromatography-mass selective detector/flame ionization detector (GC-MSD/FID,

169 Agilent Technologies, USA). Detailed cryogenically concentration steps are described

170 elsewhere (Zhang et al., 2012c). Briefly, 500 ml ambient air samples in the canister

171 were first pumped into the primarily trap with glass beads and then concentrated with

172 liquid-nitrogen cryogenic trap at -180°C. Following the primary trap was heated to

173 10°C, and all target compounds were transferred by pure helium to a secondary trap at

174 -50°C with Tenax-TA as adsorbents. Majority of H_2O and CO_2 were removed through

175 these two traps. The secondary trap then was heated to get VOCs transferred by

176 helium to a third cryo-focus trap at -170°C. After the focusing step, the third trap was

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177   rapidly heated and the VOCs were transferred to the GC-MSD/FID system. The

178   mixture were first separated by a DB-1 capillary column (60 m×0.32 mm×1.0 μm,

179   Agilent Technologies, USA) with helium as carrier gas, and then split into two ways,

180   one is a PLOT-Q column (30 m×0.32 mm×20.0 μm, Agilent Technologies, USA)

181   followed by FID detector, another is to a 0.35 m×0.10 mm I.D. stainless steel line

182   followed by MSD detection. The GC oven temperature was programmed to be

183   initially at 10°C, holding for 3 min; next increased to 120°C at 5°C min^{-1}, and then

184   10°C min^{-1} to 250°C with a final holding time of 7 min. The MSD was selected ion

185   monitoring (SIM) mode and the ionization method was electron impacting. Carbon

186   monoxide (CO) in the ambient air samples were also analyzed with an Agilent model

187   6890 gas chromatography equipped with a FID and a packed column (5Å Molecular

188   Sieve 60/80 mesh, 3 m×1/8 inch). CO was first separated by packed column, then

189   converted to CH_4 by Ni-based catalyst and finally detected by FID (Zhang et al.,

190   2016a).

191   *2.3 Quality Control and Quality Assurance*

192   Before sampling, all canisters were flushed at least five times by repeatedly

193   filling and evacuating humidified zero air. In order to check if there was any

194   contamination in the canisters, all canisters were evacuated after the cleaning

195   procedures, re-filled with pure nitrogen, stored in the laboratory for at least 24 h, and

196   then analyzed the same way as field samples to make sure that all the target VOC

197   compounds were not present.

198   Target compounds were identified based on their retention times and mass

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199 spectra, and quantified by external calibration methods. The calibration standards

200 were prepared by dynamically diluting the Photochemical Assessment Monitoring

201 Stations (PAMS) standard mixture and TO-14 standard mixture (100 ppbv, Spectra

202 Gases Inc., New Jersey, USA) to 0.5, 1, 5, 15 and 30 ppb. The calibration curves were

203 obtained by running the five diluted standards plus humidified zero air the same way

204 as the field samples. The humidified zero air was initially analyzed every day to

205 ensure the cleanness of system and then the analytical system was challenged daily

206 with a one-point (typically 1 ppb) calibration before running air samples. If the

207 response was beyond +/-10% of the initial calibration curve, recalibration was

208 performed. The method detection limits (MDL) for each VOCs species were

209 presented in Table 2.

210 *2.4 Positive Matrix Factorization (PMF)*

211   PMF is a multivariate factor analysis tool that decomposes a matrix of sample

212 data into two matrices: factor contributions (G) and factor profiles (F). The method is

213 reviewed briefly here and described in greater detail elsewhere (Paatero and Tapper,

214 1994; Paatero, 1997). PMF uses both concentration and user-provided uncertainty

215 associated with the data to weight individual points. Data values below the MDL were

216 substituted with MDL/2; missing data values were substituted with median

217 concentrations. If the concentration is less than or equal to the MDL provided, the

218 uncertainty is calculated using the equation of $Unc = 5/6 \times MDL$; if the concentration

219 is greater than the MDL provided, the uncertainty is calculated as $Unc = [(\text{Error}$

220 $\text{faction} \times \text{mixing ratio})^2 + (MDL)^2]^{1/2}$. The number of factors in PMF was initially

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221 chosen based on the result of PCA/APCS model (Zhang et al., 2012c).

3. Results and discussion

222

223 *3.1 Changing mixing ratios and compositions*

224   As mentioned above, during the period II (3-12 November) temporary emission

225 control measures were implemented to improve air quality during the 2014 APEC

226 summit. Total mixing ratios of VOCs observed at the rural site inside UCAS during

227 the period II was 11.25 ± 3.22 ppb in average, significantly lower than that of $23.41\pm$

228 5.76 ppb during period I and 21.71 ± 2.97 ppb during period III (Fig. 2). These levels

229 were less than halves of 57.45, 36.17, and 56.56 ppb observed by Li et al. (2015) at an

230 urban site in Beijing before, during and after the APEC summit, respectively.

231 However, both our measurements at a rural site in this study and the measurements at

232 an urban site by Li et al. (2015) consistently demonstrated that the temporary

233 emission control resulted in a large decrease in ambient VOCs during the APEC

234 summit, with more than 30% reduction in the urban areas (Li et al., 2015) and about

235 50% reduction in rural areas as observed in this study. This reduced ambient mixing

236 ratios of VOCs during the period II was also in line with the decreased $PM_{2.5}$

237 concentrations observed in Beijing during the APEC summit (Liu et al., 2015c), or

238 reduced NO_2 vertical column densities (VCD) and aerosol optical depth (AOD) in

239 Beijing during the APEC summit based on remote sensing (Huang et al., 2015).

240   The percentages shared by alkanes, alkenes, and ethyne in total VOCs were quite

241 similar: alkanes accounted for 54, 57 and 54% of VOCs, alkenes accounted for 12, 16

242 and 17%, and ethyne accounted for 13, 14 and 14% of VOCs during periods I, II and

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243 III, respectively. Instead, percentages shared by aromatics became lower during

244 period II (12%) when compared to that in period I (21%) or period III (15%).

245   The mean mixing ratios of alkanes, alkenes, aromatics and ethyne during period

246 II were 6.47, 1.83, 1.33, and 1.62 ppb (Fig. 2), and they decreased by 49.0, 32.5, 72.8,

247 and 48.1%, respectively, when compared to those during period I. Aromatics

248 evidently had a more substantial drop. Benzene, toluene, ethylbenzene, and

249 m,p-xylene, which are the most abundant aromatics and usually collectively termed as

250 BTEX, were 52.8, 73.1, 78.8, and 80.5% lower during period II than during period I,

251 respectively.

252   The total ozone formation potentials (OFPs) based on the maximum incremental

253 reactivity (Carter, 2009) in average during periods I, II and III were 60.64, 28.51, and

254 61.47 ppb (Table S1), respectively, with a 53.0% reduction during period II relative to

255 the period I (Fig. 2). Their secondary organic aerosol formation potentials (SOAFPs)

256 under high-NOx and low-NOx conditions (Ng et al., 2007; Lim and Ziemann, 2009)

257 were also calculated (Table S2). As showed in Fig. 2, total SOAFPs under low-NOx

258 conditions decreased by 71.0% from 8.77 μg m^{-3} during the period I to 2.54 μg m^{-3}

259 during period II, and total SOAFPs under high-NOx conditions decreased by 64.4%

260 from 4.02 μg m^{-3} during period I to 1.43 μg m^{-3} during period II. This significant

261 decrease in OFPs and SOAFPs during period II is related to lowered VOCs mixing

262 ratios, especially larger drop in reactive alkenes and aromatics: alkenes and aromatics

263 explain 26% and 52% of the reduction in total OFPs, respectively; while the decrease

264 in total SOAFPs is mostly due to changed contribution by aromatic (Table S2), whose

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265   SOAFPs decreased from 7.30 µg m^{-3} during period I to 1.93 µg m^{-3} during period II

266   under low-NOx condition, 2.39 µg m^{-3} during period I to 0.75 µg m^{-3} during period II

267   under high-NOx condition. Decrease the emissions of reactive alkenes and aromatics

268   are especially effective for OFPs and SOAFPs reduction.

269   *3.2 Pollution episodes and influence of source regions*

270   As showed in Fig. 3d and 3e, a number of episodes with mixing ratios of VOCs

271   over 30 ppb were recorded along with the increase in CO and SO$_2$ concentrations (Fig.

272   3d) during the campaign, such like that on 4-5 November, 15-16 November, 18-21

273   November, 28-30 November, 17 December, and 26-28 December. During the episode

274   on 3-5 November, for example, the total mixing ratio of VOCs was 14.30 ppb on 3

275   November, reached 31.96 ppb on 4 November, and then decreased again to 13.83 ppb

276   on 5 November. As shown in Fig. 3a, wind speeds were all below 2 m s^{-1} during 3-5

277   November, and the planetary boundary layer (PBL) height on 4 November (477 m)

278   was approximately 83% of that on 3 November (578 m) (Fig. 3c). This lower PBL

279   height on 4 November could only partly explain the higher levels of VOCs. Figure

280   S1a showed the 72-h back trajectories (HYSPLIT, ver. 4.0; http://www.arl.noaa.

281   gov/ready/hysplit4.html) of air masses from 3-5 November at the height of 100 m in

282   12-h intervals and the corresponding mixing ratios of VOCs. It demonstrated that

283   mixing ratios of VOCs increased rapidly while air masses changed from the northerly

284   to the southerly, and then declined sharply while the air masses turned back from the

285   southerly to the northerly again. The southern areas of UCAS are the central Beijing

286   with stronger emissions, consequently air masses passed through these areas would

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287 carry higher levels of pollutants to the sampling site, leading to the quick increase of

288 mixing ratios of VOCs. This rapid change of source regions could reasonably explain

289 more than the PBL height during the pollution episode of VOCs. As showed in Fig.

290 S1b, 1c, and 1d, back trajectories also suggested that the episodes on 18-21 November,

291 28-30 November and 26-28 December are related to the changed source regions.

292   According to the 72-h back trajectories, air masses arriving at the sampling site

293 could be categorized into two types (Fig. 4): 1) southerly (S) air masses, which passed

294 through Hebei, Shandong, Tianjin, and central Beijing with high-density emissions

295 before reaching UCAS; 2) northerly (N) air masses, which originated from Mongolia,

296 quickly passed through areas with less anthropogenic activity and low-density

297 emission before reaching UCAS. The pollution episodes with higher mixing ratios of

298 VOCs and CO, including the cases on 26-30 October, 4-5 November, 15-16

299 November, 18-20 November, 25-26 November and 26-28 December (Fig. 3d and 3e),

300 all occurred under the influence of southerly air masses, also suggesting the impacts

301 of emissions in the south.

302   During period I, II and III, the average mixing ratios of VOCs for southerly air

303 masses were 2.3, 2.3 and 2.9 times that for northerly air masses (Fig. 4), respectively;

304 OFPs in the southerly air masses were 2.0, 2.0 and 3.3 times that in the northerly air

305 masses, respectively; and SOAFPs in the air masses from the south were 1.7, 3.3, and

306 3.7 times that in the air masses from the north under low-NOx conditions, and 1.9, 2.7,

307 and 3.5 times that in the air masses from the north under high-NOx conditions,

308 respectively. This indicates that the north and south regions are completely different in

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309   their source strengths. Developing strict control measures in the southern region is a

310   cost-effective way for abating VOCs pollution in Beijing. For the other cities suffered

311   from ozone and $PM_{2.5}$ pollution in the world, adopt a series of control measures in

312   VOCs hotspot are essential for pollution prevention.

313   As mentioned above, the mixing ratios of VOCs, as well as their OFPs and

314   SOAPFs, decreased greatly during period II. We can further see the changes in the

315   southerly and northerly air masses to indicate the changes in different source regions.

316   In the southerly air masses, when compared to that during period I average mixing

317   ratios of alkanes, alkenes, aromatics, and ethyne during period II were 8.32, 2.16, 1.93,

318   and 2.23 ppb, with reduction rates of 46.0, 33.3, 64.3, and 44.7%, respectively;

319   accordingly, OFPs decreased by 48.1% and SOAFPs decreased by 63.5 % (low-NOx

320   conditions) and 57.6% (high-NOx conditions) during period II when compared to that

321   during period I (Fig. 4). In the northerly air masses, average mixing ratios of alkanes,

322   alkenes, aromatics, and ethyne decreased 37.7, 4.8, 87.0, and 18.4% during period II

323   when compared to that during period I, respectively; OFPs decreased by 48.9% and

324   SOAFPs decreased by over 70% during period II relative to period I (Fig. 4). As

325   discussed below, more drastic decrease in aromatics in both the northerly and

326   southerly air masses implied more effective emission control in industrial solvent use

327   during the APEC summit, and the less changes in mixing ratios of alkenes in the

328   northerly air masses were related to the less effective control of domestic

329   coal/biomass burning in the northern regions. The mixing ratios of VOCs in the

330   southerly and northerly air masses during period III were 36.1% and 7.2% higher than

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331 that during period I, respectively. This difference in the increase rates might be

332 explained by the fact that the urban areas in the south are largely central heating areas

333 where heating supply was only available since 15 November, and the northern areas

334 were largely rural areas where individual household heating might already started

335 during period I.

336 *3.3 Source attribution and apportioning*

337 *3.3.1 Indication from tracers*

338   The great changes in mixing ratios of VOCs during campaign might be resulted

339 from changed contribution by emission sources, such like enhanced emission control

340 during the APEC summit or intensified emission due to wintertime heating. These

341 changes could be indicated by characteristic fingerprints of different sources (Guo et

342 al., 2007).

343   The toluene/benzene (T/B) ratio, a widely used indicator for sources of aromatics,

344 was 1.09, 0.67 and 0.70 in average during period I, II and III, respectively (Fig. S2a).

345 While T/B ratios during periods II and III were approaching 0.6, which is

346 characteristic of coal/biomass burning (Liu et al., 2008; Liu et al., 2015d), the ratios

347 during the period I fell between that of coal/biomass burning (0.6) and vehicle exhaust

348 (1.6), which is characteristic of vehicular exhaust (Wang et al., 2002; Liu et al., 2009;

349 Zhang et al., 2013a). Carbon monoxide (CO), a typical tracer of incomplete

350 combustion of biomass or fossil fuels (Parrish et al., 2009; Zhang et al., 2015a),

351 showed highly significant correlations with benzene during the period II (r^2=0.96, Fig.

352 S2b) and the period III (r^2=0.88, Fig. S2b). SO$_2$, a good indicator of coal burning (Li

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353   et al., 2017), had similar concentrations during periods II and periods I, but its

354   concentrations increased 56.5% in average during period III compared to that during

355   period I (Fig. 3d), suggesting that coal burning contributed more after the start of

356   central heating. Methyl tert-butyl ether (MTBE), a specific indicator of gasoline

357   related traffic emission (Song et al., 2007; Cai et al., 2010), showed better correlation

358   with benzene during period I (r^2=0.88, Fig. S2c) than during period II and III.

359   As toluene, ethylbenzene and xylene (TEX), are mainly from solvent use in

360   painting, decoration and coating (Guo et al., 2007; Zhang et al., 2012c), the ratios of

361   TEX to CO were widely used to examine the impact of solvent use relative to

362   combustion emissions (Zhang et al., 2013a). The ratios of T/CO, E/CO and X/CO

363   were 0.61±0.09, 0.23±0.06 and 0.35±0.07 (ppb/ppm) during period II, obviously

364   lower when compared to that of 1.16±0.49, 0.59±0.24 and 0.99±0.41 during period

365   I, or 1.34±0.27, 0.40±0.06 and 0.83±0.09 during period III (Fig. 5B), respectively.

366   This drop in aromatics/CO ratios during period II also reflected more effective control

367   of solvent use during the APEC summit.

368   If further categorized according to the air masses trajectories, the ratios of T/CO,

369   E/CO and X/CO decreased 29.5, 45.7 and 45.7% in the southerly air masses during

370   period II relative to period I, and decreased 68.0, 80.3 and 83.0% in the northerly air

371   masses during period II relative to period I, respectively (Fig. 5A). Apparently larger

372   decrease in TEX/CO ratios in the northerly air masses reflected the control of solvent

373   use was more effective in northern regions.

374   *3.3.2 Source Apportioning by PMF*

375   Thirty-five most abundant VOCs, including alkanes, alkenes, aromatics, ethyne,

376   and sources tracers such as chloromethane, trichloroethylene, tetrachloroethylene and

377   MTBE, plus SO_2 and CO, were selected for the PMF receptor model. Figure 6 shows

378   the 5 sources retrieved by the model.

379   Factor 1 has high values of MTBE and C_5-C_6 alkanes. MTBE is a common

380   gasoline additive in China and 2,2-dimethylbutane is used to enhance the octane

381   levels of gasoline (Chang et al., 2004; Song et al., 2007; Cai et al., 2010); Ethyne can

382   be formed during fuel combustion (Blake and Rowland, 1995; Song et al., 2007;

383   Suthawaree et al., 2010); C_5-C_6 alkanes are associated with unburned vehicular

384   emissions (Guo et al., 2004; Cai et al., 2010; Zhang et al, 2013b). Consequently factor

385   1 is related to the gasoline vehicle emission.

386   Factor 2 is distinguished by a strong presence of trichloroethylene,

387   tetrachloroethylene and moderate contributions of propene and butenes.

388   Trichloroethylene and tetrachloroethylene are species from manufacturing industrials

389   (Yuan et al., 2013; Zhang et al., 2015b); propene and butenes are gases widely used by

390   industries for make organic chemicals (Guo et al., 2007), such as production of

391   synthetic rubber in the petrochemical industry (Lau et al., 2010). Thus factor 2 was

392   identified as industrial emission.

393   Factor 3 accounts for a larger percentage of the toluene, ethylbenzene,

394   m/p-xylene and o-xylene. It is known that TEX are the primary constituents of solvent

395   (Guo et al., 2004; Yuan et al., 2009; Zheng et al., 2013; Zhang et al., 2014c; Ou et al.,

396   2015). They are also main component in emissions from auto factory painting and

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397   building coating (Liu et al., 2008; Yuan et al., 2010). Therefore, this source is

398   considered as solvent use related to painting and architecture.

399   Factor 4 is diesel exhaust which is characterized by a significant amount of

400   n-undecane and n-dodecane (Song et al., 2007; Zhang et al., 2012c).

401   Factor 5 is characterized by the presence of ethane, ethylene, CO, SO_2 and

402   chloromethane. Chloromethane is the typical tracer of biomass burning (Liu et al.,

403   2008; Cai et al., 2010; Zhang et al., 2014c). Ethylene, ethane and propene are top 3

404   species of rice straw burning (Zhang et al, 2013c; Fang et al., 2017). The VOC species

405   from coal burning were mainly ethyne, C_2-C_3 alkenes and alkanes, and aromatics like

406   benzene (Liu et al., 2008). SO_2 is mainly from coal burning (Li et al., 2017). So factor

407   5 is related to the coal/biomass burning.

408   Figure 7 shows the source contributions during period I, II and III. During period

409   I gasoline exhaust was the largest source and accounted for 24.0% of VOCs, while

410   during period II coal/biomass burning became the largest source. The most significant

411   changes due to temporary emission control during the period II were in the

412   contribution percentages by coal/biomass burning (22.3% in period I and 42.4% in

413   period II) and by solvent use (21.9% in period I and 5.8% in period II). The large drop

414   in the contribution by solvent use was consistent with the above discussion about the

415   TEX/CO ratios. Quite similar contributions were observed for industrial emission and

416   diesel exhaust.

417   In the period III (13 November-31 December) with the central heating starting

418   from 15 November, coal/biomass burning became the largest source (45.1%), and

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419   industrial emission, solvent use, diesel exhaust and gasoline exhaust accounted for

420   25.2, 12.8, 8.7 and 8.2% of VOCs, respectively. The time series of source

421   contributions during the campaign were showed in Fig. S3, the contribution

422   percentages by coal/biomass burning increased gradually with the wintertime heating,

423   while that of gasoline exhaust instead decreased.

424   Coal/biomass burning was an important source of VOCs during winter in Beijing,

425   especially during period III with the start of central heating. In Beijing, coal

426   consumption was greater than that of residential biomass (Liu et al., 2016). During

427   2008-2014 in Beijing the annual residential coal consumptions increased gradually

428   while the total coal consumption decreased (Beijing Municipal Bureau of Statistics,

429   2015). The residential coal combustion is prevailing for heating and cooking by using

430   domestic coal stoves in rural areas around urban Beijing particularly during

431   wintertime. In 2014, although the annual residential coal consumption accounts for 17%

432   (2.93×10^9 kg a^{-1}) of the total coal consumption in Beijing (Beijing Municipal Bureau

433   of Statistics, 2015), residential coal burning could contribute predominately to

434   ambient VOCs from coal burning since the emission factors of VOCs from residential

435   coal burning have been found to be a factor of 20 greater than those from coal-fired

436   power plants (Liu et al., 2017).

437   Compared with that in the period I (Fig. S4), the contribution by solvent use

438   during the period II was reduced to a greater extent; it became 4.29 ppb lower and

439   could explain 37.6% of the reduction in ambient VOCs (Table S3). The contribution

440   by gasoline vehicles was 3.18 ppb lower and accounted for 27.9% of total reductions.

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441   The contribution by diesel exhaust and industrial emission reduced 2.28 ppb and 1.35

442   ppb, and explained 20.0 and 11.8% of total reduction, respectively. Coal/biomass

443   burning showed similar contributions during period I and II with an elevated

444   contribution percentage in the period II due to the reduction in other sources. This is

445   consistent with the fact that during the APEC summit residential coal/biomass burning

446   was not restricted in the rural areas. Traffic-related sources (gasoline and diesel

447   vehicles) and solvent use account for 47.9 and 37.6% of total reduction in ambient

448   VOCs, indicating that control measures (Table 1) related to the control of traffic and

449   solvent use were among the most effective ways to reduce the ambient VOCs.

450   Figure 8 shows the source contributions in the southerly and northerly air masses

451   during period I, II and III, respectively. In the southerly air masses, traffic related

452   emission (gasoline and diesel vehicles) was the largest source, contributing 44.1 and

453   41.5% of VOCs during the period I and II, respectively; while coal/biomass burning

454   instead was the largest source during period III, contributing 38.2% of VOCs. In the

455   northerly air masses, coal/biomass burning contributed 28.8, 51.6 and 48.8% of VOCs

456   during period I, II and III, respectively. Overall, gasoline vehicle exhaust contributed

457   more VOCs in the southern regions (mostly densely populated urban areas) and

458   coal/biomass burning and diesel exhaust accounted for more emissions of VOCs in

459   northern regions (mostly rural areas). Contributions of different sources to most

460   reactive alkenes and aromatics based on PMF were presented in Fig. 9. Alkenes was

461   mainly coming from coal/biomass burning with shares of 31.2-68.0%, and gasoline

462   exhaust ranked second with contributions of 3.0-26.5%. Unlike alkenes, solvent use

463 was the major contributors of aromatics, accounting 77.5% during period I and 29.0%

464 during period II in the northerly air masses; gasoline exhaust contributed 8.2-43.6% of

465 aromatics during campaign. In the southerly air masses, reductions in solvent use,

466 gasoline exhaust, and diesel exhaust during the period II relative to the period I could

467 explain 38.1, 31.1, and 15.8% of total reduction of VOCs, respectively. In the

468 northerly air masses, reductions of solvent use, diesel exhaust, and gasoline exhaust

469 during the period II relative to the period I could explain 46.5, 35.8 and 11.9% of total

470 reduction of VOCs, respectively. Consequently, control measures related to solvent

471 use and gasoline exhaust were more effective in the southern regions, while the

472 control of solvent use and diesel exhaust emission were more effective in the northern

473 region.

474 *3.3.3 Source contributions to SOAFPs*

475   With the PMF source apportioning results, the contributions of SOAFPs by

476 different sources were further estimated. As showed in Fig. 10, under low-NOx

477 condition the SOAFPs by solvent use were much higher than that by other sources,

478 which were 4.88, 0.68 and 2.89 μg m^{-3}, accounting for 56.9, 27.2 and 54.7% of total

479 SOAFPs during period I, II and III, respectively. Gasoline exhaust contributed 19.2,

480 29.5 and 10.9%, and diesel exhaust contributed 16.5, 26.8 and 11.3% of SOAFPs

481 during period I, II and III, respectively. During the period II with temporary

482 intervention measures, the reduction of SOAFPs was mainly due to reduced

483 contribution by solvent use, gasoline exhaust and diesel exhaust, which could explain

484 69.1, 14.9 and 12.2% the reduction in SOAFPs, respectively. Under high-NOx

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485   condition, calculated reduction of SOAFPs during the period II relative to the period I

486   could largely explained by reduced contributions by solvent use, diesel exhaust and

487   gasoline exhaust, which accounted for 54.0, 25.8 and 16.8% of the reduction in

488   SOAFPs, respectively.

489   It is worth noting that recent chamber studies revealed that aromatic

490   hydrocarbons or traditional VOCs could not fully explain SOA formed from

491   atmospheric aging of source emissions (Zhao et al., 2014; 2015; Liu et al., 2015a;

492   Deng et al., 2017; Fang et al., 2017), particularly for emissions from diesel vehicles or

493   biomass burning (Zhao et al., 2015; Deng et al., 2017; Fang et al., 2017). Therefore

494   the discussion on SOAFPs in this study is only limited to traditional anthropogenic

495   SOA precursor species (mainly aromatic hydrocarbons), and intermediate-volatility

496   organic compounds (IVOCs), which is a large of secondary organic aerosol (Zhao et

497   al., 2014), should be further considered in order to fully understand the influence of

498   control measures on the ambient SOAs.

499   **4. Conclusions**

500   During severe wintertime haze events in recent years in Beijing, SOA often

501   shared higher factions in organic aerosols, yet their precursor VOCs in ambient air

502   during winter are much less understood especially in the rural areas. In this study we

503   collected ambient air samples from 25 October to 31 December in 2014 at a rural site

504   inside the campus of UCAS in north Beijing. As the APEC summit was held in

505   Beijing during 5-11 November 2014 and temporary control measures were adopted to

506   improve the air quality and in fact the so-called "APEC Blue" was achieved due to the

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507   enhanced emission control. Therefore we could take advantage of this opportunity to

508   see how the control measures influence the ambient VOCs in the rural areas. On the

509   other hand, wintertime heating with coal burning has been regarded as major

510   contributor to wintertime PM pollution and haze events, thus we could also compare

511   the ambient VOC levels and compositions before and after the start of central heating

512   on 15 November, and investigate the influence of central heating on ambient VOCs

513   based on our observation at the rural site.

514   We observed that during the enhanced emission control period II (3-12

515   November) average mixing ratios of VOCs decreased ~50% when compared to that

516   before or after that period. And their ozone and SOA formation potentials accordingly

517   decreased by ~50% and ~70%, respectively as a result of temporary intervention

518   measures implemented during period II. The larger drop in SOA formation potentials

519   was attributable to more effective control of aromatic hydrocarbons mainly from

520   solvent use. Based on PMF source apportioning, the control of traffic-related

521   emissions (gasoline and diesel exhaust) and solvent use could explain 47.9 and 37.6%

522   of the reduction in ambient VOCs. This result thus offered an observation-based

523   evaluation about the temporary emission control measures.

524   With back trajectory analysis, we could compare ambient VOCs with the change

525   of wind directions and thus further investigate source emission strength in different

526   regions. Total mixing ratios of VOCs in the southerly air masses were 2.3, 2.3 and 2.9

527   times that in the northerly air masses before, during and after the period with

528   temporary emission control for the APEC summit. VOC episodes during the

529   campaign all occurred under southerly winds. This confirms that emission control in

530   the southern urbanized regions is crucial for reducing ambient VOCs.

531   As residential coal/biomass burning were not controlled during the APEC

532   summit, its contribution to the ambient mixing ratios of VOCs was similar between

533   period I and period II, although contribution percentages by coal/biomass burning

534   became the largest in average due to drops in the percentages by other sources. During

535   period III with central heating, coal/biomass burning became the largest source that

536   accounted for 45.1% of the VOCs. Specifically, during period III coal/biomass

537   combustion contributed 38.2% of VOCs in the southerly air masses (or in the south

538   regions), and 48.8% of VOCs in the northerly air masses (or in the north regions).

539   The finding of this study will provide useful information on the direction of

540   control strategies of VOCs for abating both ozone and $PM_{2.5}$ pollution. The reduction

541   in total OFPs and SOAFPs during the APEC is largely due to the drop of reactive

542   alkenes and aromatics, so adopting reactivity-based emission control would be the

543   effective and economical way to lower the ozone and SOA formation potentials of

544   VOCs. As control measures related to solvent use and vehicle exhausts explained

545   most of the reduction in both ambient VOCs and their ozone/SOA formation

546   potentials, enhancing emission control for solvent use (especially solvents with

547   aromatic hydrocarbons) and vehicle exhaust would benefit improving air quality in

548   the future. Moreover, as observed in this study, even in megacities like Beijing,

549   burning raw coal or biomass for household heating in winter could contribute near

550   half of VOCs in ambient air, therefore a cleaner way of wintertime household heating

551 would help to lower both primary emission and secondary formation of air pollutants.

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895

896   Table 1. Enhanced temporary air pollution control measures during the 2014
897   Asian-Pacific Economic Cooperation (APEC) summit

Control types	Details	Control areas
Traffic	1. Yellow label vehicles were banned to run inside the sixth ring of Beijing and the Huairou urban area; 2. The number of private vehicles in operation reduced by 50% through an odd/even-number-plate rule throughout Beijing; 3. Trucks were limited to drive inside the sixth ring of Beijing between 6 am and 24 pm; 4. 70% of government cars also ordered off the roads in Beijing.	Inside the sixth ring of Beijing and the Huairou urban area
Industrial	1. 9289 enterprises were suspended, 3900 enterprises were ordered to limit production; 2. More than 40000 construction sites were shut down.	Beijing, some areas of Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia
Other fields	1. Open fire was completely controlled at North China Plain; 2. Increasing road cleaning and water spraying in Beijing; 3. Other relate control measures carried out in surrounding areas.	North China Plain Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia

898

899 Table 2. The mixing ratios, ranges and 95% confidence intervals (95% C.I.) of VOCs

900 during period I, II and III at the rural site inside UCAS (in parts per trillion by volume,

901 pptv).

Species	MDL[a]	Period I		Period II		Period III	
		Range	Mean (95% C.I.)	Range	Mean (95% C.I.)	Range	Mean (95% C.I.)
Ethane	39	1172-7855	3254(743)	910-5511	2442(491)	1082-12714	3674(465)
Propane	31	427-6145	2880(720)	270-4138	1296(384)	598-7604	2479(329)
i-Butane	14	53-2755	1121(312)	59-1400	474(187)	106-2741	754(129)
n-Butane	21	158-2947	1283(302)	83-1735	562(196)	174-3047	841(136)
i-Pentane	14	94-3729	1425(354)	39-1388	561(167)	72-12590	1018(279)
n-Pentane	8	47-1697	615(182)	30-910	247(106)	26-4808	456(112)
2,2-Dimethylbutane	14	15-68	30(6)	17-32	24(3)	BDL[b]-75	26(2)
Cyclopentane	12	13-135	64(15)	BDL-64	35(7)	13-274	50(8)
2,3-Dimethylbutane	12	13-140	45(15)	22-51	32(4)	13-235	38(6)
2-Methylpentane	8	13-679	171(68)	12-257	77(31)	9-1077	124(27)
3-Methylpentane	7	12-548	150(54)	14-220	68(26)	16-792	104(20)
n-Hexane	6	115-1033	505(97)	102-921	324(89)	108-7393	1400(257)
Methylcyclopentane	9	10-283	100(30)	13-195	59(23)	BDL-535	88(17)
2,4-Dimethylpentane	4	BDL-43	15(5)	BDL-15	10(2)	BDL-90	16(2)
Cyclohexane	6	10-458	167(51)	10-107	43(14)	7-646	76(17)
2-Methylhexane	6	10-304	68(27)	7-56	22(6)	7-318	51(10)
2,3-Dimethylpentane	9	BDL-139	31(12)	BDL-24	15(2)	BDL-102	28(3)
3-Methylhexane	6	12-436	93(38)	8-97	41(11)	9-367	70(12)
2,2,4-Trimethylpentane	9	12-126	44(12)	BDL-41	25(4)	BDL-127	38(5)
n-Heptane	10	12-358	89(33)	12-71	30(8)	13-441	82(14)
Methylcyclohexane	5	BDL-162	51(17)	BDL-66	21(7)	BDL-162	44(8)
2,3,4-Trimethylpentane	6	BDL-38	14(4)	BDL-12	9(1)	BDL-59	16(2)
2-Methylheptane	4	8-175	31(16)	BDL-31	13(3)	BDL-91	22(3)
3-Methylheptane	5	BDL-231	26(20)	BDL-15	8(1)	BDL-74	17(2)
n-Octane	6	8-104	42(11)	BDL-31	18(3)	BDL-160	40(6)
n-Nonane	6	9-99	40(11)	BDL-37	18(4)	BDL-171	38(6)
n-Decane	6	14-777	129(74)	8-110	36(14)	BDL-600	73(17)
n-Undecane	7	47-317	151(35)	27-206	66(20)	11-374	94(12)
n-Dodecane	7	9-646	129(57)	25-313	75(30)	8-316	63(9)
Ethylene	41	367-3495	1788(391)	553-3572	1254(352)	319-13911	2313(428)
Propene	31	117-1264	430(118)	170-766	371(67)	176-3222	820(128)
1-Butene	17	19-161	107(18)	BDL-100	55(12)	19-581	137(22)
1,3-Butadiene	20	21-403	154(44)	23-234	79(27)	BDL-2140	252(74)
trans-2-Butene	5	BDL-41	18(4)	BDL-35	12(4)	BDL-425	39(10)
cis-2-Butene	7	9-50	23(4)	BDL-38	14(5)	BDL-276	37(7)
1-Pentene	20	BDL-47	33(3)	21-25	23(1)	BDL-127	52(6)
Isoprene	13	BDL-623	163(56)	16-143	62(15)	17-765	200(24)
trans-2-Pentene	10	BDL-37	17(4)	BDL-19	15(3)	BDL-65	23(3)
cis-2-Pentene	6	BDL-24	11(3)	BDL-9	8(0)	BDL-46	15(2)
2-Methyl-2-butene	12	13-50	21(4)	17-20	18(1)	BDL-61	24(2)
Benzene	14	75-2695	868(279)	43-1465	410(179)	72-2916	795(151)
Toluene	9	120-3585	1273(419)	47-1186	343(126)	62-3425	840(146)
Ethylbenzene	6	25-2210	684(240)	12-611	145(67)	23-2450	317(75)
m/p-Xylene	9	39-2106	765(248)	16-620	149(67)	25-3285	422(91)
Styrene	8	15-578	167(71)	BDL-99	32(11)	10-1267	151(38)
o-Xylene	4	11-965	334(104)	9-284	71(31)	15-1224	178(36)
Isopropylbenzene	4	5-66	24(7)	BDL-21	11(2)	BDL-77	18(3)
n-Propylbenzene	4	6-231	71(27)	BDL-55	20(7)	5-239	38(8)
m-Ethyltoluene	3	13-593	136(67)	4-91	28(11)	4-854	85(23)
p-Ethyltoluene	3	6-295	61(29)	4-59	17(6)	4-245	41(9)
1,3,5-Trimethylbenzene	3	7-217	48(21)	BDL-35	12(4)	4-179	38(6)
o-Ethyltoluene	3	5-246	64(26)	4-58	17(6)	5-230	40(8)
1,2,4-Trimethylbenzene	6	22-984	220(93)	13-219	58(22)	8-803	127(26)
1,2,3-Trimethylbenzene	5	12-442	82(37)	BDL-92	24(9)	6-300	56(11)
1,3-Diethylbenzene	4	11-135	35(12)	BDL-26	15(3)	BDL-126	26(4)
1,4-Diethylbenzene	4	14-461	80(40)	5-69	23(7)	BDL-292	51(10)
1,2-Diethylbenzene	4	BDL-30	15(4)	BDL-8	6(1)	BDL-76	15(2)
Ethyne	57	406-10539	3128(1043)	290-6260	1625(615)	584-10378	3008(509)

902 [a] MDL, method detection limits, pptv; [b] BDL, bellowed detection limit.

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905 Figure1. Location of sampling site at a rural inside the campus of University of

906 Chinese Academy of Science (UCAS).

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908
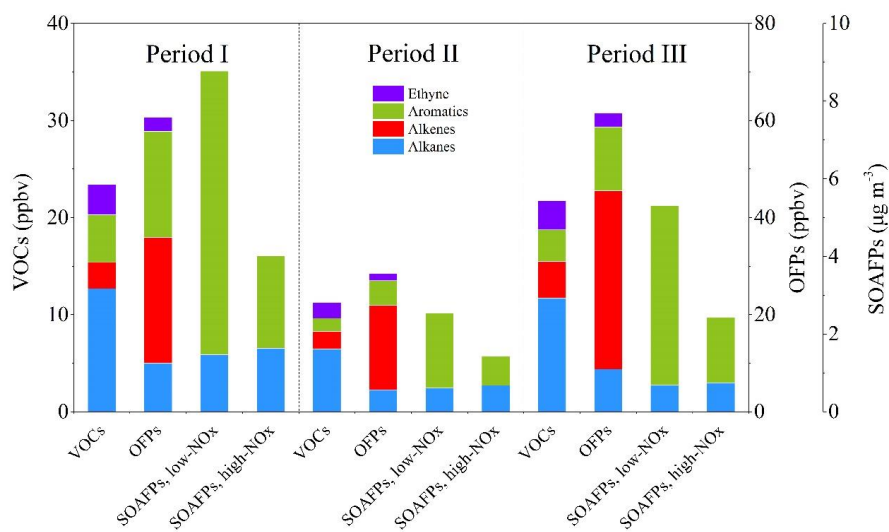
Figure 2. Mixing ratios of VOCs, ozone formation potentials (OFPs) and secondary

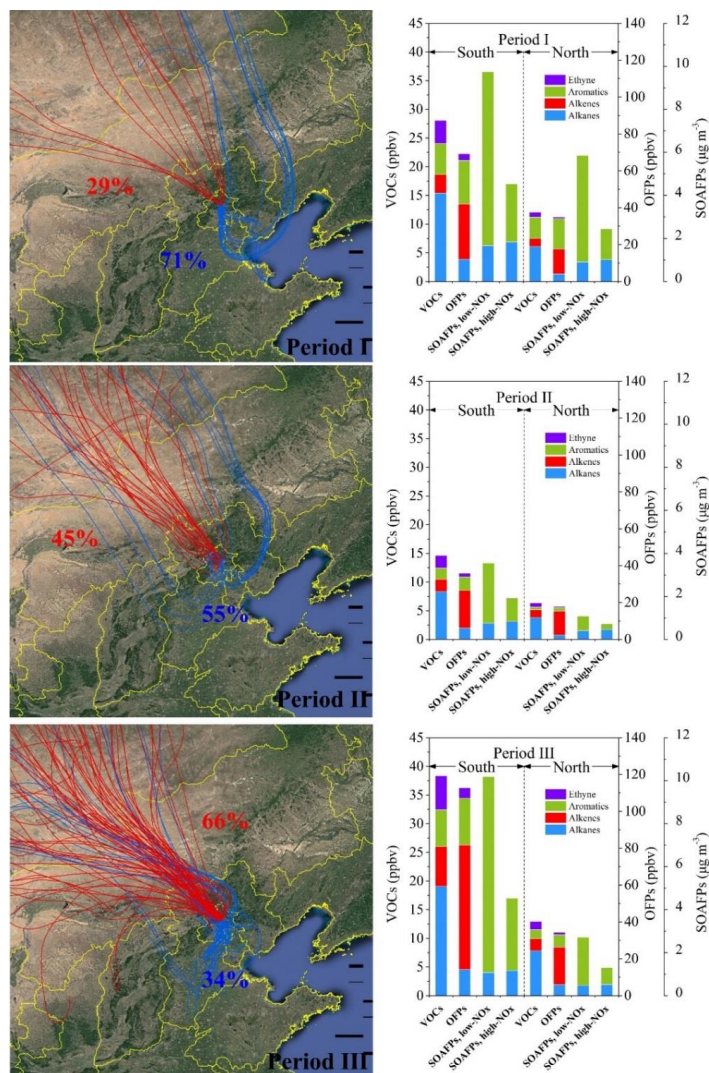organic aerosol formation potentials (SOAFPs) during period I, II and III at UCAS,

respectively.

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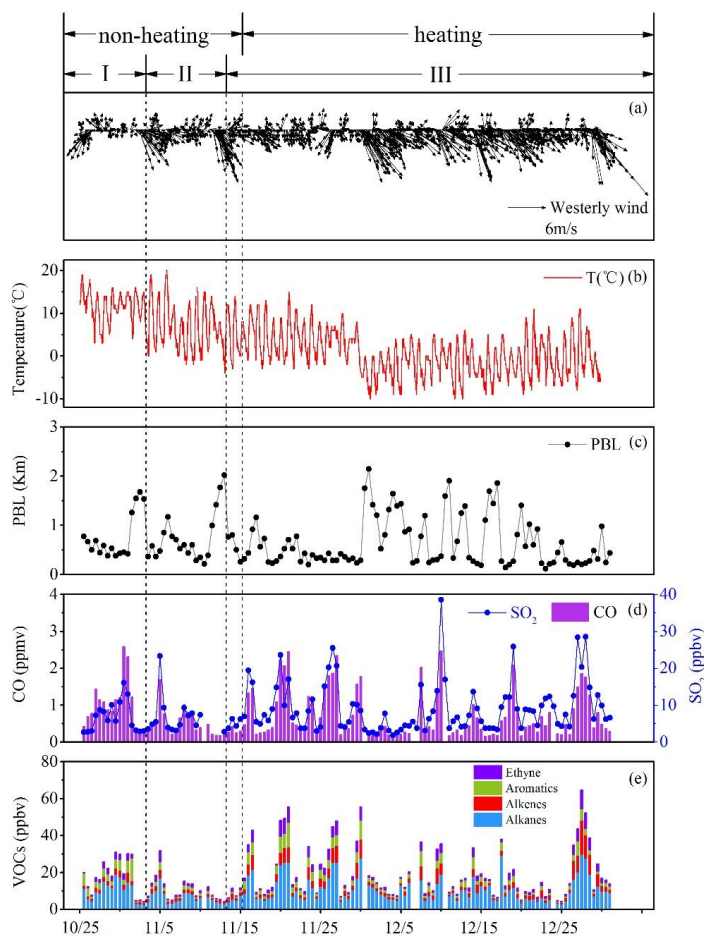
Figure 3. Time series of (a) wind speed and wind direction, (b) temperature, (c) planetary boundary layer height, (d) mixing ratios of CO and SO$_2$, (e) mixing ratios of VOCs, at the sampling site inside UCAS. The heating periods started on 15 November. Period I: 25 October-2 November; Period II: 3-12 November; Period III: 13 November-31 December.

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Figure 4. Mixing ratios of VOCs, ozone formation potentials (OFPs) and secondary

organic aerosol formation potentials (SOAFPs) in the air masses from the south and

north regions (right) and corresponding back trajectories at 100 meters above the

ground level during period I, II and III, respectively (Left).

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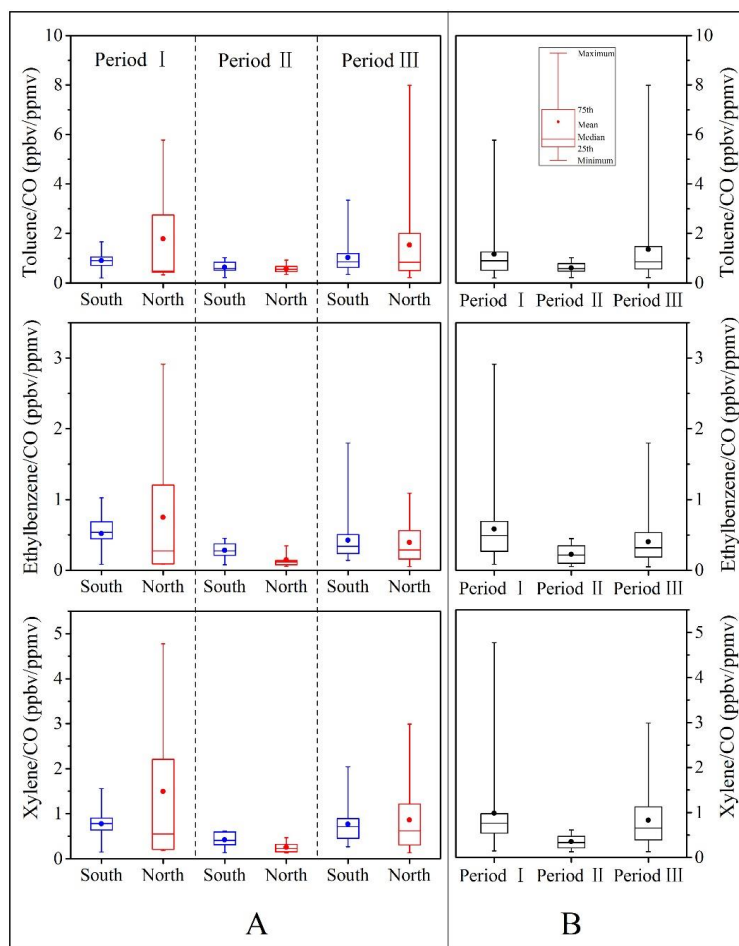
926

927 Figure 5. Ratios of aromatic hydrocarbons to carbon monoxide (CO) (A) in the air

928 masses from the south and north regions and (B) in all samples during period I, II and

929 III. (The lower and upper boundaries of the box represent the 25th and 75th

930 percentiles, respectively; the whiskers below and above the box indicate the minimum

931 and maximum, respectively; the line within the box marks the median; the dot
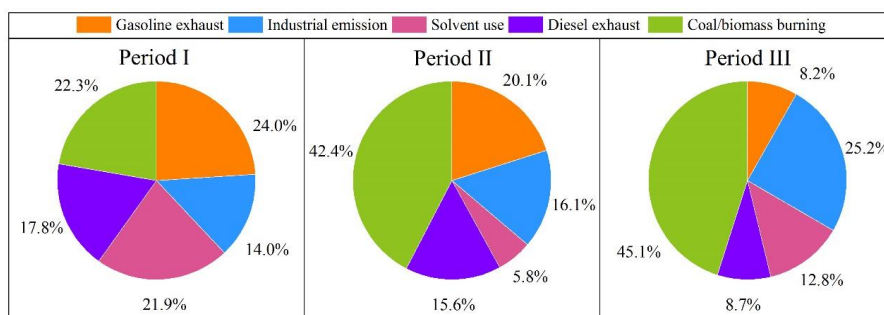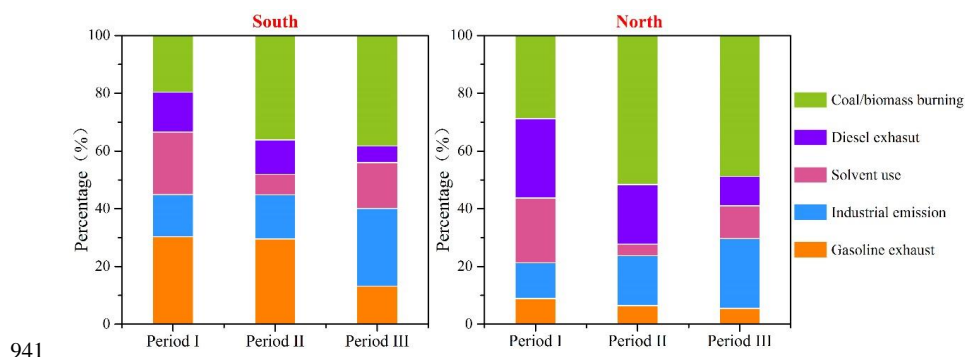
932 represent the mean).

933
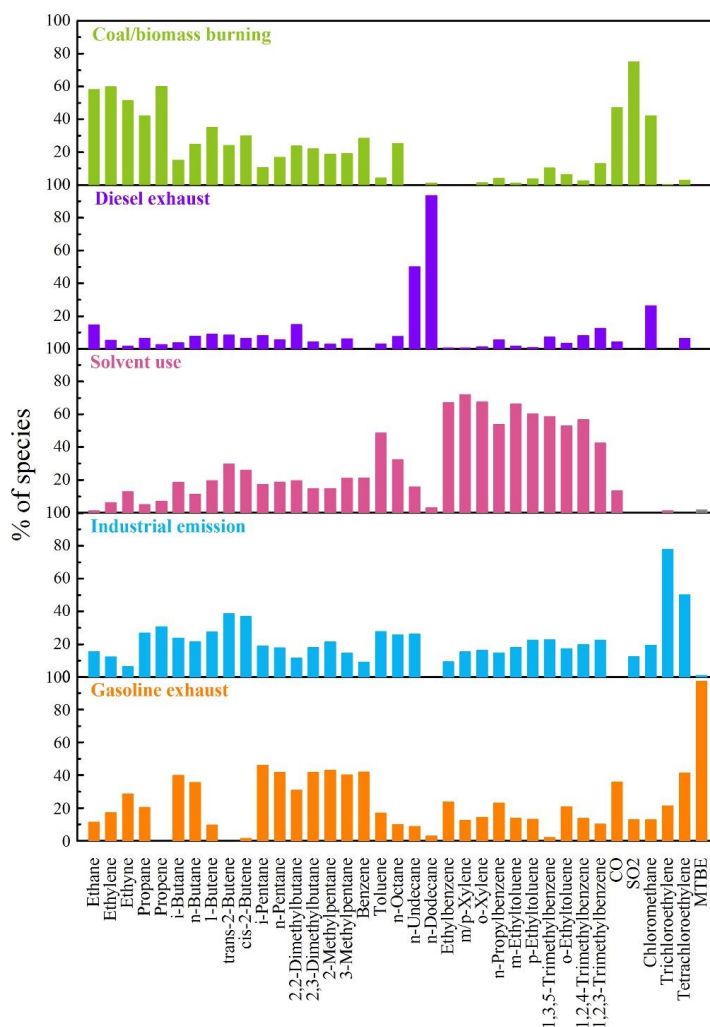
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935   Figure 6. Source profiles revolved by PMF.

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Figure 7. Contributions to VOCs in percentages (%) by different sources during period I, II and III.

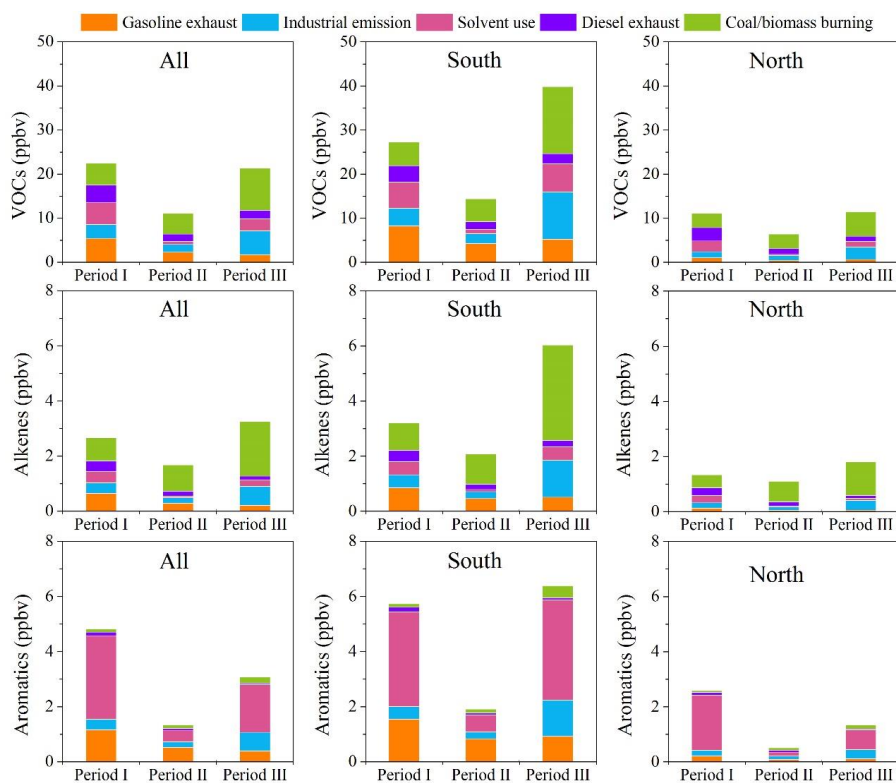Figure 8. Sources contributions (%) to VOCs in the air masses from the south and north regions during period I, II and III.

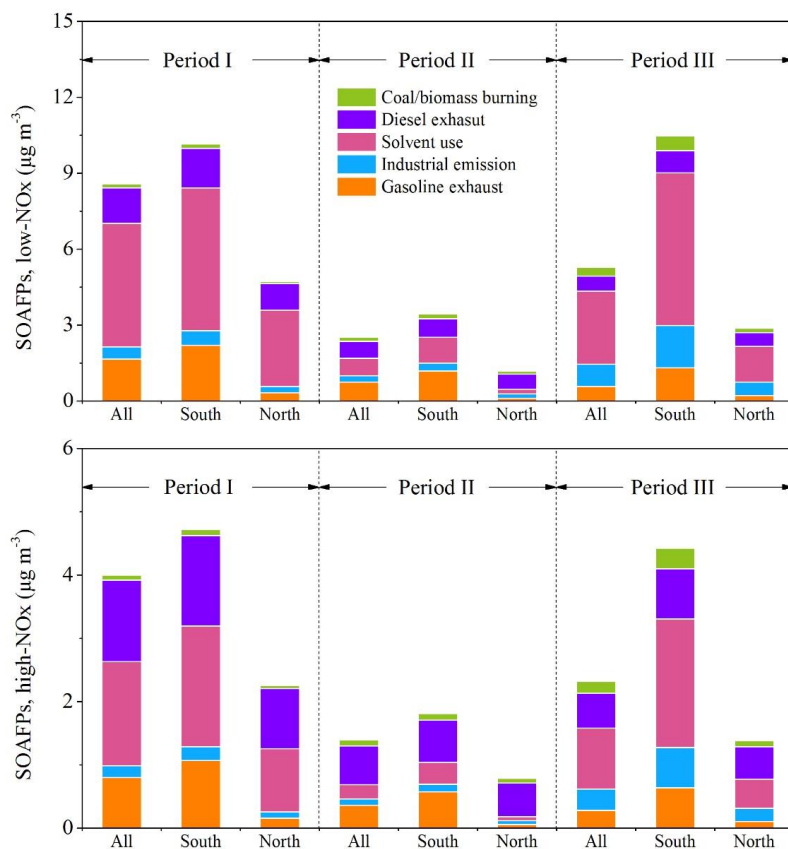Atmospheric
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946 Figure 9. Sources contributions of VOCs and reactive alkenes/aromatics at UCAS, in

947 all samples and in air masses from the south and north regions during period I, II and

948 III.

949

950

951 Figure 10. Contributions to SOAFPs by different sources in the air masses from the

952 south and north regions during period I, II and III.