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

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Abstract

32

33　　While residential coal/biomass burning might be a major and underappreciated

34　emission source for $PM_{2.5}$ especially during winter season, it is not well constrained

35　whether burning solid fuels contributes substantially to ambient volatile organic

36　compounds (VOCs), which are precursors to secondary organic aerosols (SOA) that

37　typically have a higher contribution to particulate matters during winter haze events.

38　In this study, ambient air samples were collected in 2014 from 25 October to 31

39　December at a rural site on the campus of the University of Chinese Academy of

40　Sciences (UCAS) in northeastern Beijing for the analysis of VOCs. Since temporary

41　intervention measures were implemented on 3-12 November to improve the air

42　quality for the Asian-Pacific Economic Cooperation (APEC) summit held on 5-11

43　November in Beijing, and wintertime central heating started on 15 November in

44　Beijing after the APEC summit, this sample collection period provided a good

45　opportunity to study the influence of temporary control measures and wintertime

46　heating on ambient VOCs. As a result of the temporary intervention measures

47　implemented during 3-12 November (period II), the total mixing ratios of

48　non-methane hydrocarbons averaged 11.25 ppb, approximately 50% lower than the

49　values of 23.41 ppb in period I (25 October-2 November) and 21.71 ppb in period III

50　(13 November-31 December). The ozone and SOA formation potentials decreased by

51　~50% and ~70%, respectively, during period II relative to period I, with the larger

52　decrease in SOA formation potentials attributed to more effective control over

53　aromatic hydrocarbons mainly from solvent use. Back trajectory analysis revealed that

54　the average mixing ratios of VOCs in southerly air masses were 2.3, 2.3 and 2.9 times

those in northerly air masses during periods I, II and III, respectively; all VOC

episodes occurred under the influence of southerly winds, suggesting much stronger

emissions in the southern urbanized regions than in the northern rural areas. Based on

a positive matrix factorization (PMF) receptor model, the altered contributions from

traffic emissions and solvent use could explain 47.9% and 37.6% of the reduction in

ambient VOCs, respectively, during period II relative to period I, indicating that the

temporary control measures on vehicle emissions and solvent use were effective at

lowering the ambient levels of VOCs. Coal/biomass burning, gasoline exhaust, and

industrial emissions were among the major sources, and they altogether contributed

60.3%, 78.6% and 78.7% of the VOCs during the periods I, II and III, respectively.

Coal/biomass burning, mostly residential coal burning, became the dominant source,

accounting for 45.1% of the VOCs during the wintertime heating period, with a

specifically lower average contribution percentage in southerly air masses (38.2%)

than in northerly air masses (48.8%). The results suggests that emission control in the

industry and traffic sectors is more effective in lowering ambient reactive VOCs in

non-heating seasons; however, during the winter heating season reducing emissions

from residential burning of solid fuels would be of greater importance and would have

health co-benefits from lowering both indoor and outdoor air pollution.

1. Introduction

Volatile organic compounds (VOCs) are precursors of tropospheric ozone and secondary organic aerosols (SOA) (Forstner et al., 1997; Odum et al., 1997; Atkinson, 2000; O'Dowd et al., 2002; Sato et al., 2010). As ozone formation in urban areas is largely VOC-limited (Shao et al., 2009; Tang et al., 2010) and SOA are important components of fine particles or $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) (Cabada et al., 2004; Lonati et al., 2005; Huang et al., 2014), reducing emissions of VOCs would be very important for improving the air quality in megacities, such as China's capital city Beijing, where air pollution has become an widespread concern, with increasing surface ozone levels during summer and severe $PM_{2.5}$ pollution during winter (Streets et al., 2007; Ji et al., 2012; Wang et al., 2014).

While exposure to indoor air pollution from burning solid fuels affects nearly half of the world's population and household air pollution has long been a major environmental cause of death (Martin et al., 2011; Lim et al., 2012; Subramanian, 2014), emissions from residential energy use such as heating and cooking, prevalent in India and China, also have the largest impact on global premature mortality from outdoor air pollution (Lelieveld et al., 2015). In fact, Juda-Rezler et al. (2011) showed that coal combustion in residential boiler during winter was a major source of PM_{10} in four cities of central eastern European. A recent study revealed that even in Beijing and its surrounding regions, residential use of solid fuels might be a major and underappreciated ambient pollution source for $PM_{2.5}$ (particularly BC and OC) during

96   winter heating period (Liu et al., 2016). Since substantial amounts of VOCs are

97   released from poor-technology burning of coal and biomass/biofuels (Yokelson et al.,

98   2008; Shrivastava et al., 2015; Fang et al., 2017; Liu et al., 2017; Cheng et al., 2018),

99   it is of wide concern how residential use of solid fuels, particularly for wintertime

100   household heating, would influence ambient levels and compositions of VOCs. In

101   residential areas of Izmir, Turkey, for example, household burning of coal on

102   uncontrolled burners for domestic heating during winter was found to be a larger

103   source of VOCs than the local traffic (Sari and Bayram, 2014).

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

105   emission inventories of VOCs, to formulate emission control measures on reducing

106   ambient VOCs is a highly challengeable task. More field measurements are therefore

107   needed to characterize VOCs in ambient air and in emission sources for better source

108   attribution. In Beijing, for example, since higher levels of ozone mostly occur during

109   hot seasons, many field measurements of VOCs were conducted in summer with a

110   focus on their sources (Song et al., 2007; Lu et al., 2007; Yuan et al., 2009; Wang et

111   al., 2010a) and their mixing ratios (Liu et al., 2009; An et al., 2012; Zhang et al.,

112   2012a; Liu et al., 2013), particularly during ozone episodes. On the other hand, during

113   extremely severe and persistent haze events in Beijing, organic matter (OM) could

114   contribute 30-70% of the total $PM_{2.5}$ with higher fractions of SOA in OM (Guo et al.,

115   2014; Huang et al., 2014; Zhang et al., 2014a). However, the effect of VOCs on

116   wintertime $PM_{2.5}$ pollution is much less understood, although the control of VOCs, as

117   SOA precursors, is also of great importance in the control of $PM_{2.5}$ air pollution. A

118 previous study already demonstrated that levels of aromatic hydrocarbons and

119 carbonyls increased significantly on haze days in urban Beijing from 2008 to 2010

120 (Zhang et al., 2014b), yet few reports are available about wintertime precursor VOCs,

121 especially about the potential contribution by burning solid fuels for household

122 heating.

123   Apart from health benefits from lowering indoor air pollution, controlling

124 emissions in the residential sector would be of greater importance to further improve

125 outdoor air quality worldwide in the future (Liu et al., 2016), although previously

126 efforts have been overwhelmingly targeted on reducing emissions from industrial and

127 traffic sectors in many regions. In northern China, for example, air quality has been

128 greatly improved in recent years due to the implementation of long-term pollution

129 control actions (Hao and Wang, 2005; Wang et al., 2009; Zhang et al., 2012b; Liu et

130 al., 2015a; Kelly and Zhu, 2016). However, the air quality there is not satisfactory

131 compared to that in cities in the United States and Europe, especially in winter, with

132 frequent haze events and high $PM_{2.5}$ levels. Consequently, during critical international

133 events such as the 2008 Olympic Games (Wang et al., 2010b; Huang et al., 2010) and

134 the 2014 Asia-Pacific Economic Cooperation (APEC) summit, temporary intervention

135 measures were adopted to guarantee better air quality. This type of temporary

136 intervention provided a good opportunity to assess the relatively importance of

137 different sources and to study the effectiveness of various control measures on the

138 reduction of ambient air pollutants including VOCs (Yao et al., 2013; Huang et al.,

139 2017). For the 21th Asia-Pacific Economic Cooperation (APEC) summit held in

140 Beijing on 5-11 November 2014, temporary control measures in Beijing and its

141 surrounding regions resulted in significant decreased in air pollutants, including $PM_{2.5}$

142 and NOx (Huang et al., 2015; Liu et al., 2015b; Wang et al., 2015; Xu et al., 2015;

143 Zhang et al., 2016a). For the VOCs in ambient air, as observed by Li et al. (2015) at

144 an urban site on the campus of Peking University, the total mixing ratios of VOCs

145 were reduced by 44% during the APEC summit control period compared to those in

146 the period before. As the 2008 Olympic Games or the 2014 APEC were all held in the

147 non-heating periods, it is not certain in what extent the temporary intervention

148 measures mostly targeted on industrial and traffic emissions would take effect in the

149 winter heating period.

150 While vehicle exhaust is an important source of VOCs in urban areas (McDonald

151 et al., 2015; Liu et al., 2015c; Ortega et al., 2016; Deng et al., 2017; Gentner et al.,

152 2017), coal burning and biomass/biofuel burning may also contribute substantially to

153 VOCs particularly in winter when raw coal and biofuels are widely used for

154 household heating in regions like the northern China (Liu et al., 2016; Zhang et al.,

155 2016b; Liu et al., 2017). In fact, a study by Wang et al. (2013) in 2011-2012 revealed

156 that even at an urban site in Beijing, coal combustion could account for 28-39% of the

157 VOCs observed in ambient air. As raw coal and/or biofuel burning widely occur in

158 rural areas in winter (Liu et al., 2016), it is necessary to investigate extensively on

159 how enhanced emissions due to wintertime household heating would influence

160 ambient VOCs particularly in rural areas, as forming SOA or ozone is an issue of

161 regional scale.

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

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

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

165   wintertime heating period starting from 15 November. The objectives of the present

166   study are: (1) to study changes in the mixing ratios and composition of VOCs at a

167   rural site in Beijing in response to the emission control during the APEC summit and

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

169   changes during the PM-polluted winter; (3) to evaluate the impact of control measures

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

171   rural areas; and (4) to assess the contribution of residential use of solid fuels for

172   household heating to ambient VOCs during winter.

173   **2. Methodology**

174   *2.1 Sampling Site and Field Sampling*

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

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

177   district of Beijing. UCAS is located approximately 60 km northeast of the central of

178   Beijing and approximately 150 km northwest of the city of Tianjin. It is surrounded

179   by several small villages and farmlands. The samples were collected about 16 meters

180   above the ground on the top of a four-story building, approximately 100 m west of a

181   national road and only 1.5 km away from the main APEC conference hall.

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

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

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

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

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

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

188 days when the visibility was less than 10 km at a relative humidity of less than 90%

189 (Fu et al., 2016). A total of 153 samples were collected during sampling. According to

190 the air pollution control measures, the field campaign was divided into periods I (25

191 October-2 November), II (3-12 November) and III (13 November-31 December).

192 Period   II   was   when   temporary   control   measures   (Table   1;

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

194 better air quality. Wintertime heating started on 15 November just after the cease of

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

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

197 speeds were 3.5, 3.9, and 4.1 m s^{-1}; and the average temperature was 11.4, 7.0, and

198 0.6 °C during periods I, II and III, respectively.

199 *2.2 Laboratory Analysis of VOCs and Carbon Monoxide*

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

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

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

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

204 elsewhere (Zhang et al., 2012c). Briefly, 500 ml ambient air in the canister was first

205 drawn through a primary liquid-nitrogen cryogenic trap with glass beads at -160°C to

206 get VOCs trapped. The primary trap was then heated to 10°C, and all target

207 compounds were transferred by pure helium to a secondary trap at -50°C with

208 Tenax-TA as adsorbents. Majority of H_2O and CO_2 were removed through these two

209 traps. Then the secondary trap was heated to get VOCs transferred by helium to a

210 third cryo-focus trap at -170°C. After the focusing step, the third trap was rapidly

211 heated and the VOCs were transferred to the GC-MSD/FID system. The mixture were

212 first separated by a DB-1 capillary column (60 m×0.32 mm×1.0 μm, Agilent

213 Technologies, USA) with helium as carrier gas, and then split into two ways, one is a

214 PLOT-Q column (30 m×0.32 mm×20.0 μm, Agilent Technologies, USA) followed by

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

216 MSD detection. The GC oven temperature was programmed to be initially at 10°C,

217 holding for 3 min; increase to 120°C at 5°C min^{-1}, and then at 10°C min^{-1} to 250°C

218 with a final holding time of 7 min. The MSD was run in selected ion monitoring (SIM)

219 mode and the ionization method was electron impacting. Carbon monoxide (CO) in

220 the ambient air samples were analyzed with an Agilent model 6890 gas

221 chromatography equipped with a FID and a packed column (5Å Molecular Sieve

222 60/80 mesh, 3 m×1/8 inch). CO was first separated by packed column, then converted

223 to CH_4 by Ni-based catalyst and finally detected by FID (Zhang et al., 2016b).

224 *2.3 Quality Control and Quality Assurance*

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

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

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

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

229 then analyzed the same way as field samples to make sure that all the target VOCs

230 were not present.

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

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

233 were prepared by dynamically diluting the Photochemical Assessment Monitoring

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

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

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

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

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

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

240 responses were beyond ±10% of the initial calibration curve, recalibration was

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

242 presented in Table 2.

243 *2.4 Positive Matrix Factorization (PMF)*

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

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

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

247 1994; Paatero, 1997). PMF uses both concentration and user-provided uncertainty

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

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

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

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

252 is greater than the MDL provided, the uncertainty is calculated as $Unc =$ [(Error

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

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

255 **3. Results and discussion**

256 *3.1 Changing mixing ratios and compositions*

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

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

259 summit. The total mixing ratio of VOCs observed at the rural site at UCAS during the

260 period II was 11.25±3.22 ppb on average, significantly lower than the value of

261 23.41±5.76 ppb during period I and 21.71±2.97 ppb during period III (Fig. 2). These

262 levels were less than half the values (57.45, 36.17, and 56.56 ppb) observed by Li et al.

263 (2015) at an urban site in Beijing before, during and after the APEC summit,

264 respectively. However, our measurements at a rural site in this study and the

265 measurements at an urban site by Li et al. (2015) consistently demonstrated that the

266 temporary emission control resulted in a large decrease in ambient VOCs during the

267 APEC summit, with a more than 30% reduction in urban areas (Li et al., 2015) and an

268 approximately 50% reduction in rural areas, as observed in this study. This reduced

269 ambient mixing ratios of VOCs during the period II was also in line with the

270 decreased PM$_{2.5}$ concentrations observed in Beijing during the APEC summit (Liu et

271 al., 2015b), and the reduced NO$_2$ vertical column density (VCD) and aerosol optical

272 depth (AOD) in Beijing during the APEC summit based on remote sensing (Huang et

273 al., 2015).

274   The percentages of alkanes, alkenes, and ethyne in total VOCs were similar:

275 alkanes accounted for 54, 57 and 54% of VOCs; alkenes accounted for 12, 16 and

276 17%; and ethyne accounted for 13, 14 and 14% of VOCs during periods I, II and III,

277 respectively. Instead, the percentages of aromatics was lower during period II (12%)

278 than during period I (21%) and period III (15%).

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

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

281 48.1% lower than those during period I, respectively. Aromatics evidently underwent

282 a more substantial decrease. Benzene, toluene, ethylbenzene, and m,p-xylene, which

283 are the most abundant aromatics and usually collectively termed BTEX, were 52.8,

284 73.1, 78.8, and 80.5% lower during period II than during period I, respectively.

285   Table S1 shows a comparison of VOCs from our study with those observed at

286 other metropolitan areas in the world. Mixing ratios of VOCs from this study at a

287 rural site in Beijing during period I (23.41 ppb) and period III (21.71 ppbv) were

288 comparable to that in urban Shanghai from January 2007 to March 2010 (Cai et al.,

289 2010), but lower than those in Beijing during June 2008 (Wang et al., 2010a),

290 Guangzhou from June 2011 to May 2012 (Zou et al., 2015), Lille, French from May

291 1997 to April 1999 (Borbon et al., 2002) and Houston in August-September 2006

292 (Leuchner and Rappengluck, 2010). Average mixing ratios of VOCs during period II

293 (11.25 ppbv) with enhanced emission control in the present study were significantly

294 lower than those reported in other metropolitan areas. As for the most abundant VOC

295 species including ethane, propane, ethylene, benzene, toluene and ethyne, the mixing

296 ratios of ethane and ethylene at UCAS were similar to that at Beijing during June

297 2008 (Wang et al., 2010a) and urban Guangzhou from June 2011 to May 2012 (Zou et

298 al., 2015), but significantly lower than that in urban Beijing during 2014 APEC (Li et

299 al., 2015). Mixing ratios of propane in present study are comparable to that in Hong

300 Kong from September 2002 to August 2003 (Guo et al., 2007) and Lille, French from

301 May 1997 to April 1999 (Borbon et al., 2002), but factors of 2-3 lower than that

302 reported in urban Shanghai from January 2007 to March 2010 (Cai et al., 2010) and

303 Guangzhou from June 2011 to May 2012 (Zou et al., 2015). Mixing ratios of benzene

304 and toluene in Lille, French from May 1997 to April 1999 (Borbon et al., 2002) were

305 over 2 times higher than that in present study. Mixing ratios of ethylene, benzene and

306 toluene in present study were comparable to those observed in Houston during

307 August-September 2006 (Leuchner and Rappengluck, 2010), meanwhile ethyne, a

308 tracer of incomplete combustion, had mixing ratios 3-4 times higher than that in

309 Houston.

310   The total ozone formation potential (OFP), based on the simplified approach of

311 MIR (maximum incremental reactivity) scale (Carter, 2009), on average was 60.64,

312 28.51, and 61.47 ppb (Table S2) during periods I, II and III, respectively, with a 53.0%

313 reduction during period II relative to the period I (Fig. 2). The secondary organic

314 aerosol formation potential (SOAFP) under high-NOx and low-NOx conditions (Ng et

315 al., 2007; Lim and Ziemann, 2009) were also calculated (Table S3). As shown in Fig.

316 2, the total SOAFP under low-NOx conditions decreased by 71.0% from 8.77 μg m^{-3}

317 during the period I to 2.54 μg m^{-3} during period II, and the total SOAFP under

318 high-NOx conditions decreased by 64.4% from 4.02 μg m^{-3} during period I to 1.43 μg

319 m^{-3} during period II. This significant decrease in OFP and SOAFP during period II is

320 related to lowered VOC mixing ratios, especially larger decreases in reactive alkenes

321 and aromatics: alkenes and aromatics explain 26% and 52% of the reduction in total

322 OFP, respectively, while the decrease in total SOAFP is mostly due to the altered

323 contribution of aromatics (Table S3), whose SOAFP decreased from 7.30 μg m^{-3}

324 during period I to 1.93 μg m^{-3} during period II under low-NOx conditions and from

325 2.39 μg m^{-3} during period I to 0.75 μg m^{-3} during period II under high-NOx conditions.

326 The results suggest that enhancing the emission control of reactive alkenes and

327 aromatics would be more effective for reducing OFPs and SOAFPs of ambient VOCs.

328 *3.2 Pollution episodes and influence of source regions*

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

330 over 30 ppb were recorded along with an increase in the CO and SO$_2$ concentrations

331 (Fig. 3d) during the campaign, such as those on 4-5 November, 15-16 November,

332 18-21 November, 28-30 November, 17 December, and 26-28 December. During the

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

334 on 3 November, reached 31.96 ppb on 4 November, and then decreased again to 13.83

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

336 during 3-5 November, and the planetary boundary layer (PBL) height on 4 November

337 (477 m) was approximately 83% of that on 3 November (578 m) (Fig. 3c). This lower

16

338 PBL height on 4 November could only partly explain the higher levels of VOCs.

339 Figure S2a shows the 72-h back trajectories (HYSPLIT, ver. 4.0; http://www.arl.noaa.

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

341 12-h intervals and the corresponding mixing ratios of VOCs. It demonstrated that the

342 mixing ratios of VOCs increased rapidly while air masses changed from northerly to

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

344 to northerly. The southern areas of UCAS are in central Beijing where emissions are

345 stronger; consequently, air masses that passed through these areas would carry higher

346 levels of pollutants to the sampling site, leading to the quick increase in the mixing

347 ratios of VOCs. This rapid change in source regions could reasonably explain more

348 than the PBL height during the pollution episode of VOCs. As shown in Fig. S2b, 2c,

349 and 2d, back trajectories also suggested that the episodes on 18-21 November, 28-30

350 November and 26-28 December are related to the altered source regions.

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

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

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

354 before reaching UCAS, and 2) northerly (N) air masses, which originated from

355 Mongolia and quickly passed through areas with less anthropogenic activity and

356 low-density emissions before reaching UCAS. The pollution episodes with higher

357 mixing ratios of VOCs and CO, including the cases on 26-30 October, 4-5 November,

358 15-16 November, 18-20 November, 25-26 November and 26-28 December (Fig. 3d

359 and 3e), all occurred under the influence of southerly air masses, also suggesting the

360 impacts of emissions in the south.

361 During periods I, II and III, the average mixing ratios of VOCs for southerly air

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

363 the OFPs in southerly air masses was 2.0, 2.0 and 3.3 times that in northerly air

364 masses, respectively; and the SOAFPs in air masses from the south was 1.7, 3.3, and

365 3.7 times that in air masses from the north under low-NOx conditions and 1.9, 2.7,

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

367 respectively. These results indicate that the northern and southern regions are

368 completely different in their source strengths. Stricter control measures in the

369 southern region would be an effective way for abating VOCs pollution in Beijing.

370 As mentioned above, the mixing ratios of VOCs, as well as their OFP and

371 SOAPF, decreased greatly during period II. The changes in the southerly and

372 northerly air masses indicate the changes in emissions from different source regions.

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

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

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

376 accordingly, the OFP decreased by 48.1% and the SOAFP decreased by 63.5%

377 (low-NOx conditions) and 57.6% (high-NOx conditions) during period II compared to

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

379 alkanes, alkenes, aromatics, and ethyne decreased 37.7, 4.8, 87.0, and 18.4% during

380 period II compared to that during period I, respectively; the OFP decreased by 48.9%

381 and SOAFP decreased by over 70% during period II relative to those in period I (Fig.

382 4). As discussed below, a more drastic decrease in aromatics in both the northerly and

383 southerly air masses implied more effective control over emissions from industrial

384 solvent use during the APEC summit, and the much less changes in the mixing ratios

385 of alkenes in the northerly air masses were related to the less effective control over

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

387 the southerly and northerly air masses during period III were 36.1% and 7.2% higher

388 than those during period I, respectively. Those different increases rates might be

389 explained by the fact that the urban areas in the south were largely central heating

390 areas where heat sources were only available after 15 November and the northern

391 areas were largely rural areas where individual household heating might have started

392 during period I.

393 *3.3 Source attribution and apportionment*

394 *3.3.1 Indication from tracers*

395 The great changes in the mixing ratios of VOCs during the campaign might have

396 resulted from the altered contributions from emission sources, such as enhanced

397 emission control during the APEC summit or intensified emissions due to wintertime

398 heating. These changes could be indicated by the characteristic fingerprints of

399 different sources (Guo et al., 2007).

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

401 was 1.09, 0.67 and 0.70 on average during periods I, II and III, respectively (Fig. S3a).

402 While the T/B ratios during periods II and III approached 0.6, which is characteristic

403 of coal/biomass burning (Liu et al., 2008; Liu et al., 2015d), the ratios during period I

404   fell between that of coal/biomass burning (0.6) and vehicle exhaust (1.6) (Wang et al.,

405   2002; Liu et al., 2009; Zhang et al., 2013a). Carbon monoxide (CO), a typical tracer

406   of the incomplete combustion of biomass or fossil fuels (Parrish et al., 2009; Zhang et

407   al., 2015a), showed highly significant correlations with benzene during period II

408   (r^2=0.96, Fig. S3b) and period III (r^2=0.88, Fig. S3b). SO_2, a good indicator of coal

409   burning (Li et al., 2017), had similar concentrations during period II and period I, but

410   its concentration increased 56.5% on average during period III compared to that

411   during period I (Fig. 3d), suggesting an increased contribution of coal burning after

412   the start of central heating. Methyl tert-butyl ether (MTBE), a specific indicator of

413   gasoline related traffic emissions (Song et al., 2007; Cai et al., 2010), showed better

414   correlation with benzene during period I (r^2=0.88, Fig. S3c) than during periods II and

415   III.

416   As toluene, ethylbenzene and xylene (TEX) mainly originate from solvent use in

417   paint, decorations and coatings (Guo et al., 2007; Zhang et al., 2012c), the ratios of

418   TEX to CO are widely used to examine the impact of solvent use relative to

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

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

421   lower than the values of 1.16±0.49, 0.59±0.24 and 0.99±0.41 during period I and of

422   1.34±0.27, 0.40±0.06 and 0.83±0.09 during period III (Fig. 5B), respectively. This

423   decrease in the ratios of aromatics to CO during period II also reflected more effective

424   control over solvent use during the APEC summit.

425   If further categorized according to the air mass trajectories, the ratios of T/CO,

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

427 period II relative to those in period I, and decreased 68.0, 80.3 and 83.0% in the

428 northerly air masses during period II relative to those in period I, respectively (Fig.

429 5A). A larger decrease in the TEX/CO ratios in northerly air masses reflects the fact

430 that the control of solvent use was more effective in northern regions.

431 *3.3.2 Source Apportionment by PMF*

432 The 35 most abundant VOCs, including alkanes, alkenes, aromatics, and ethyne,

433 and source tracers, such as chloromethane, trichloroethylene, tetrachloroethylene and

434 MTBE, plus SO_2 and CO, were selected for use with the PMF receptor model. Figure

435 6 shows the 5 sources retrieved by the model.

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

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

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

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

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

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

442 1 is related to gasoline vehicle emissions.

443 Factor 2 is distinguished by a strong presence of trichloroethylene and

444 tetrachloroethylene and moderate contributions by propene and butenes.

445 Trichloroethylene and tetrachloroethylene are species from industrial manufacturing

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

447 industry to prepare organic chemicals (Guo et al., 2007), such as during the

448 production of synthetic rubber in the petrochemical industry (Lau et al., 2010). Thus,

449 factor 2 was identified as industrial emissions.

450 Factor 3 accounts for larger percentages of toluene, ethylbenzene, m/p-xylene

451 and o-xylene. TEX is known to be the primary constituent of solvent (Guo et al., 2004;

452 Yuan et al., 2009; Zheng et al., 2013; Zhang et al., 2014c; Ou et al., 2015). These

453 compounds are also the main components in emissions from automobile factories,

454 paint and building coatings (Liu et al., 2008; Yuan et al., 2010). Therefore, this source

455 is considered to be solvent use related to painting and architecture.

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

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

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

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

460 2008; Cai et al., 2010; Zhang et al., 2014c). Ethylene, ethane and propene are the top

461 3 species emitted during rice straw burning (Zhang et al, 2013c; Fang et al., 2017).

462 The VOC species from coal burning are mainly ethyne, C_2-C_3 alkenes and alkanes,

463 and as well as aromatics such as benzene (Liu et al., 2008). SO_2 is mainly from coal

464 burning (Li et al., 2017). Thus, factor 5 is related to coal/biomass burning.

465 Figure 7 shows the source contributions during periods I, II and III. During

466 period I, gasoline exhaust was the largest source and accounted for 24.0% of the

467 VOCs, while during period II, coal/biomass burning became the largest source. The

468 most significant changes due to the temporary emission control during period II were

469 in the contribution percentages of coal/biomass burning (22.3% in period I and 42.4%

470   in period II) and solvent use (21.9% in period I and 5.8% in period II). The large

471   decrease in the contribution from solvent use was consistent with the above discussion

472   about the TEX/CO ratios.

473   In period III (13 November-31 December), with central heating starting on 15

474   November, coal/biomass burning became the largest source (45.1%), and industrial

475   emission, solvent use, diesel exhaust and gasoline exhaust accounted for 25.2, 12.8,

476   8.7 and 8.2% of the VOCs, respectively. The time series of source contributions

477   during the campaign are shown in Fig. S4; the contribution percentage of

478   coal/biomass burning increased gradually with the increase in wintertime heating,

479   while that of gasoline exhaust decreased.

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

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

482   consumption was greater than that of residential biomass (Liu et al., 2016). Coal is

483   consumed in residential, industrial and power sectors in Beijing. As showed in Fig.

484   S5a, while annual total coal consumptions dropped rapidly during 2006-2015, the

485   annual residential coal consumptions remained almost unchanged with their

486   percentages in total coal consumptions rising from 8.7% in 2006 to 23.4% in 2015

487   (Beijing Municipal Bureau of Statistics, 2016; Yu et al., 2018). As a matter of fact,

488   over 60% of the residential coal consumption occurred in rural areas of Beijing (Fig.

489   S5b), and residential coal is mainly burned in the cool winter season for house heating

490   (Xue et al., 2016). While emission factors of VOCs from residential coal burning have

491   been found to be a factor of 20 greater than those from coal-fired power plants (Liu et

492 al., 2017), the differences in coal quality between the urban and rural areas augment

493 emissions in rural areas: coal used in urban area was entirely anthracite with

494 comparatively much lower emissions of volatiles than other types of coal (Xu et al.,

495 2017); instead only 5-15% of coal used in rural area was anthracite (Xue et al., 2016).

496 Consequently, residential coal combustion could have been a major contributor to the

497 ambient VOCs in rural areas of Beijing during winter.

498   Compared with that in the period I (Fig. S6), the contribution from solvent use

499 during period II was reduced to a greater extent than other sources; it became 4.29

500 ppb lower and could explain 37.6% of the reduction in ambient VOCs (Table S4). The

501 contribution from gasoline vehicles was 3.18 ppb lower and accounted for 27.9% of

502 the total reductions. The contribution from diesel exhaust and industrial emissions

503 decreased 2.28 ppb and 1.35 ppb and explained 20.0 and 11.8% of the total reduction,

504 respectively. Coal/biomass burning made similar contributions during periods I and II,

505 with an elevated contribution percentage in period II due to the reduction in other

506 sources. This is consistent with the fact that during the APEC summit residential

507 coal/biomass burning was not restricted in the rural areas. Traffic-related sources

508 (gasoline and diesel vehicles) and solvent use accounted for 47.9 and 37.6% of the

509 total reduction in ambient VOCs, indicating that control measures (Table 1) related to

510 the control of traffic and solvent use were among the most effective ways to reduce

511 ambient VOCs.

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

513 during periods I, II and III. In the southerly air masses, traffic related emission

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514 (gasoline and diesel vehicles) were the largest source, contributing 44.1 and 41.5% of

515 the VOCs during periods I and II, respectively, while coal/biomass burning was the

516 largest source during period III, contributing 38.2% of the VOCs. In the northerly air

517 masses, coal/biomass burning contributed 28.8, 51.6 and 48.8% of the VOCs during

518 periods I, II and III, respectively. Overall, gasoline vehicle exhaust contributed more

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

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

521 northern regions (mostly rural areas). The contributions of different sources to most

522 reactive alkenes and aromatics based on PMF was presented in Fig. 9. Alkenes mainly

523 originated from coal/biomass burning, with shares of 31.2-68.0%, and gasoline

524 exhaust ranked second, with contributions of 3.0-26.5%. Unlike alkenes, aromatics

525 were mainly from solvent use, accounting for 77.5% during period I and 29.0%

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

527 the aromatics during the campaign. In the southerly air masses, the reductions in

528 solvent use, gasoline exhaust, and diesel exhaust during period II relative to period I

529 could explain 38.1, 31.1, and 15.8% of the total reduction in VOCs, respectively. In

530 the northerly air masses, reductions in solvent use, diesel exhaust, and gasoline

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

532 the total reduction in VOCs, respectively. Consequently, control measures related to

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

534 the control of solvent use and diesel exhaust emissions were more effective in the

535 northern region.

536 *3.3.3 Source contributions to the SOAFP*

537   With the PMF source apportionment results, the contributions of the SOAFP of

538 different sources were further estimated. As shown in Fig. 10, under low-NOx

539 conditions, the SOAFP of solvent use was much higher than that of other sources,

540 which was 4.88, 0.68 and 2.89 μg m^{-3}, accounting for 56.9, 27.2 and 54.7% of the

541 total SOAFP during periods I, II and III, respectively. Gasoline exhaust contributed

542 19.2, 29.5 and 10.9%, and diesel exhaust contributed 16.5, 26.8 and 11.3% of the

543 SOAFP during periods I, II and III, respectively. During period II, with temporary

544 intervention measures, the reduction in SOAFP was mainly due to reduced

545 contributions from solvent use, gasoline exhaust and diesel exhaust, which could

546 explain 69.1, 14.9 and 12.2% of the reduction in SOAFP, respectively. Under

547 high-NOx conditions, the calculated reduction in SOAFP during period II relative to

548 period I could largely be explained by the reduced contributions from solvent use,

549 diesel exhaust and gasoline exhaust, which accounted for 54.0, 25.8 and 16.8% of the

550 reduction in SOAFP, respectively.

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

552 hydrocarbons and traditional VOCs could not fully explain the SOA formed during

553 atmospheric aging of source emissions (Zhao et al., 2014; 2015; Liu et al., 2015c;

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

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

556 the discussion on the SOAFP in this study is limited to traditional anthropogenic SOA

557 precursor species (mainly aromatic hydrocarbons), and intermediate-volatility organic

558 compounds (IVOCs), which are important SOA precursors (Zhao et al., 2014), should

559 be further considered in order to fully understand the influence of control measures on

560 ambient SOA.

561 **4. Conclusions**

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

563 composed higher fractions of organic aerosols, yet their precursor VOCs in ambient

564 air during winter are not well understood, especially in rural areas. In this study, we

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

566 on the campus of UCAS in north Beijing. The APEC summit was held in Beijing on

567 5-11 November 2014, temporary control measures were adopted to improve the air

568 quality, and the so-called "APEC Blue" was achieved due to the enhanced emission

569 control. Therefore, we took advantage of this opportunity to see how the control

570 measures influenced the ambient VOCs in rural areas. On the other hand, wintertime

571 heating from coal burning has been regarded as a major contributor to wintertime PM

572 pollution and haze events; thus, we also compared the ambient VOC levels and

573 composition before and after the start of central heating on 15 November, and

574 investigated the influence of wintertime heating on ambient VOCs based on our

575 observation at a rural site.

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

577 November), the average mixing ratios of VOCs decreased ~50% compared to those

578 before or after that period. In addition, the ozone and SOA formation potential

579 accordingly decreased by ~50% and ~70%, respectively, as a result of the temporary

580 intervention measures implemented during period II. The larger decrease in SOA

581 formation potentials was attributable to more effective control over aromatic

582 hydrocarbons mainly from solvent use. Based on PMF source apportionment, the

583 control of traffic-related emissions (gasoline and diesel exhaust) and solvent use could

584 explain 47.9 and 37.6% of the reduction in ambient VOCs. This result thus offered an

585 observation-based evaluation of the temporary emission control measures.

586   Through back trajectory analysis, we could compare ambient VOCs with the

587 change in wind direction and thus further investigate the source emission strengths in

588 different regions. The total mixing ratios of VOCs in southerly air masses were 2.3,

589 2.3 and 2.9 times those in northerly air masses before, during and after the period with

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

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

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

593   As residential coal/biomass burning was not controlled during the APEC summit,

594 its contribution to the ambient mixing ratios of VOCs was similar between period I

595 and period II, although the contribution percentages of coal/biomass burning became

596 the largest on average due to decreases in the percentages of other sources. During

597 period III, with emissions from burning solid fuels for household heating,

598 coal/biomass burning became the largest source, accounting for 45.1% of the VOCs.

599 Specifically, during period III, coal/biomass combustion contributed 38.2% of the

600 VOCs in southerly air masses (or in the southern regions), and 48.8% of the VOCs in

601 northerly air masses (or in the northern regions).

602   The finding of this study will provide useful information for the emission control

603   strategy of VOCs. A comparison of VOCs between period I (without intervention

604   measures) and period II (with intervention measures) revealed that the temporary

605   intervention measures mostly targeted on the control in traffic and industry (industrial

606   processes and solvent use) sectors are very effective to reduce reactive alkenes and

607   aromatics and thereby to reduce the OFPs and SOAFPs of VOCs in ambient air.

608   Therefore, enhancing emission control for solvent use (especially solvents with

609   aromatic hydrocarbons) and vehicle exhaust would benefit reducing the VOC-related

610   air pollution. However, as observed in this study, even in megacities like Beijing,

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

612   half of VOCs in ambient air. If the emission control over residential burning of solid

613   fuels is underappreciated, the intervention measures targeted on traffic and industry

614   sectors would be not so effective in the wintertime heating period as did in

615   non-heating periods either to lower $PM_{2.5}$ as indicated by Liu et al. (2016) or to lower

616   VOCs in ambient air as indicted by this study. If fact, a study by Yu et al. (2018)

617   during the same field campaign of this study demonstrated that, without emission

618   control over residential burning of solid fuels, ambient $PM_{2.5}$-bound toxic polycyclic

619   aromatic hydrocarbons in rural Beijing during the 2014 APEC summit remained

620   unchanged despite of the temporary intervention control measures, and they were

621   largely aggravated after the start of wintertime heating. Therefore, cleaner energy use

622   instead of poor-technology burning of solid fuels for household heating would have

623   tremendous health benefits in lowering both indoor and outdoor air pollution

624 particularly in heavily polluted winter. It worth noting that this study was conducted

625 in a rural area of the megacity Beijing. Emission from residential burning of solid

626 fuels would be a source of greater importance and thus deserves more concern in less

627 developed regions.

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1038 Table 1. Enhanced temporary air pollution control measures during the 2014
1039 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;	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.	
Industrial	1)	9289 enterprises were suspended, 3900 enterprises were ordered to limit production;	Beijing, some areas of Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia
	2)	More than 40000 construction sites were shut down.	
Other fields	1)	Open fire was completely controlled at North China Plain;	North China Plain
	2)	Increasing road cleaning and water spraying in Beijing;	Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia
	3)	Other relate control measures carried out in surrounding areas.	

1040

1041 Table 2. The mixing ratios, ranges and 95% confidence intervals (95% C.I.) of VOCs

1042 during period I, II and III at the rural site inside UCAS (in parts per trillion by volume,

1043 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)

1044 [a] MDL, method detection limits, pptv; [b] BDL, bellowed detection limit.
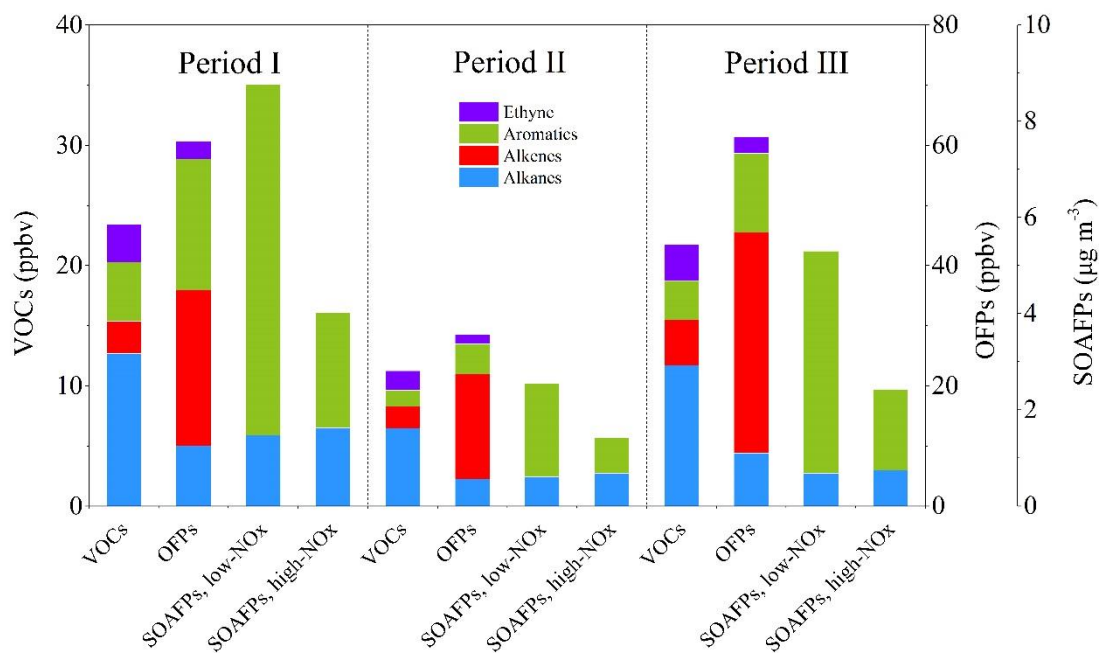
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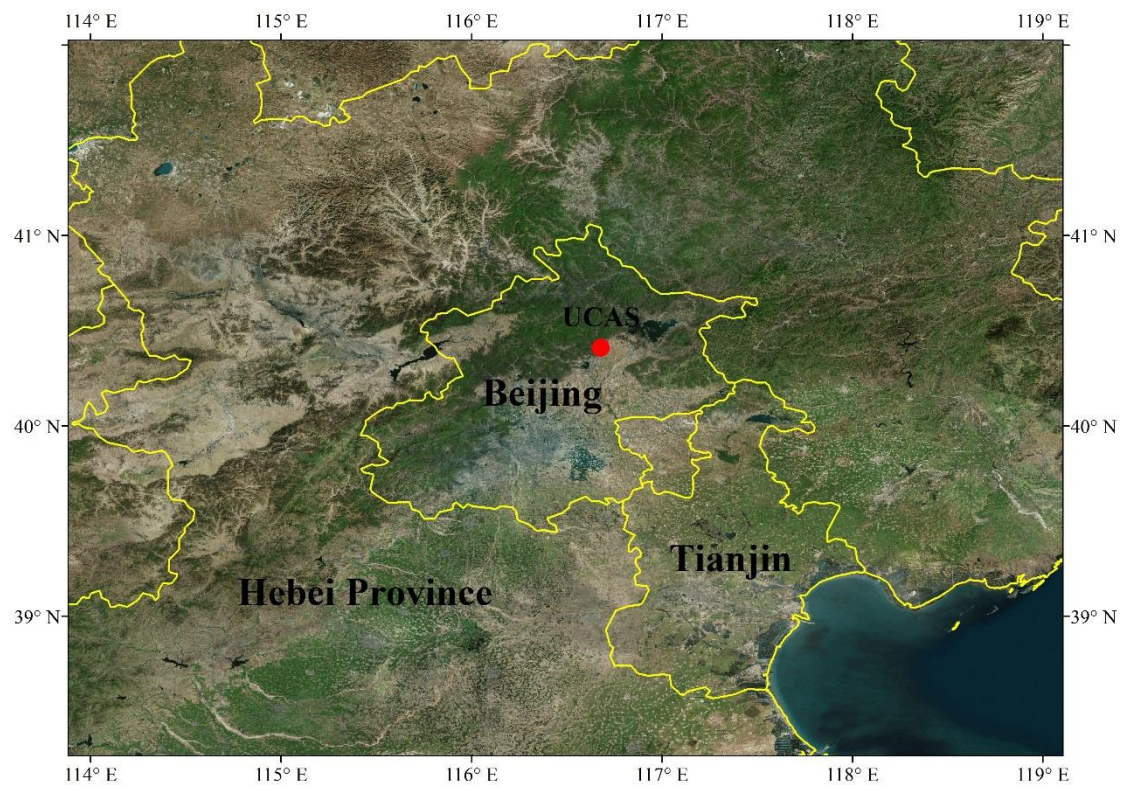
Figure1. Location of the rural sampling site inside the campus of University of Chinese Academy of Science (UCAS) in the north of Beijing.
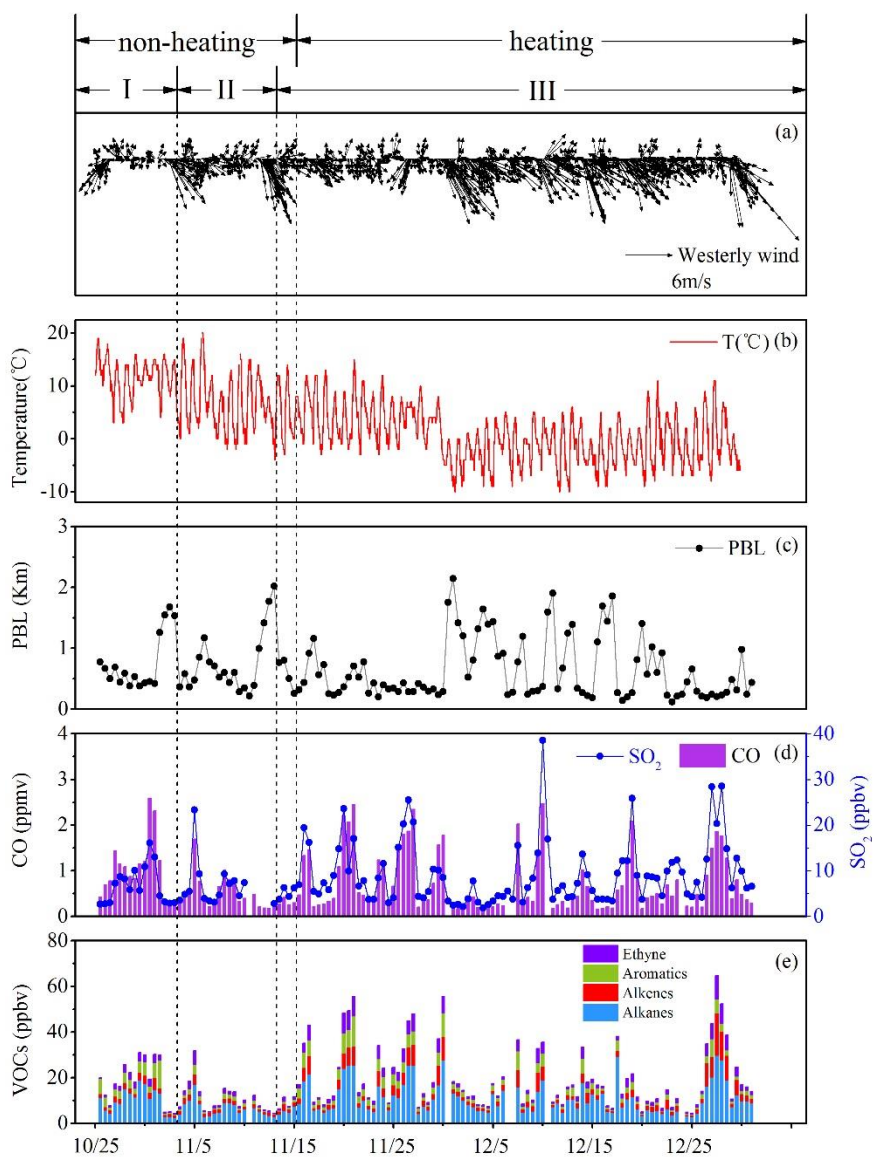
1050

1051 Figure 2. Mixing ratios of VOCs, ozone formation potentials (OFPs) and secondary

1052 organic aerosol formation potentials (SOAFPs) of ambient VOCs during period I, II
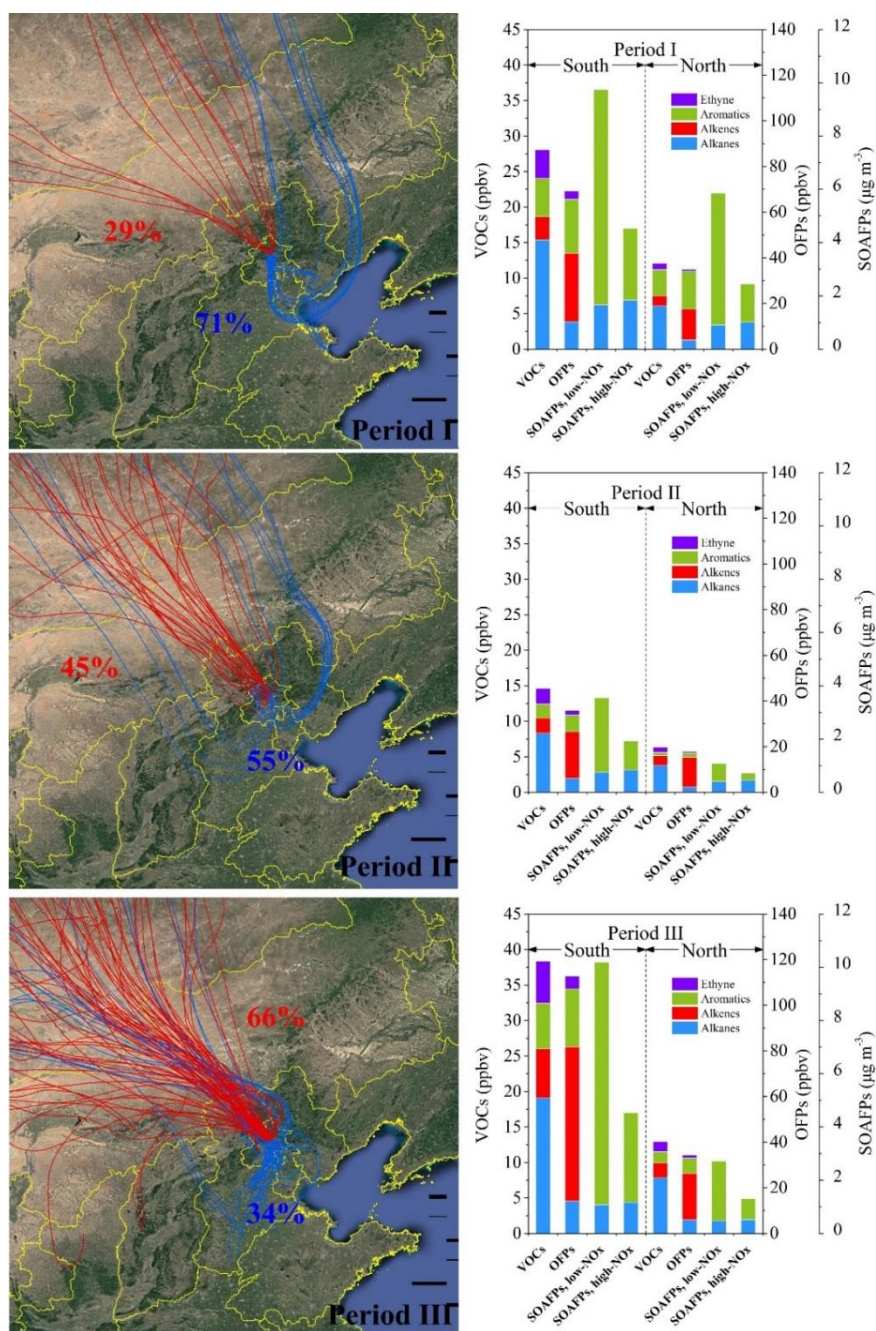
1053 and III at UCAS, respectively.

1054

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.

1062

1063 Figure 4. Mixing ratios of VOCs, ozone formation potentials (OFPs) and secondary

1064 organic aerosol formation potentials (SOAFPs) of VOCs in the air masses from the

1065 south and north regions (right) and corresponding back trajectories at 100 meters

1066 above the ground level during period I, II and III, respectively (Left).

1067
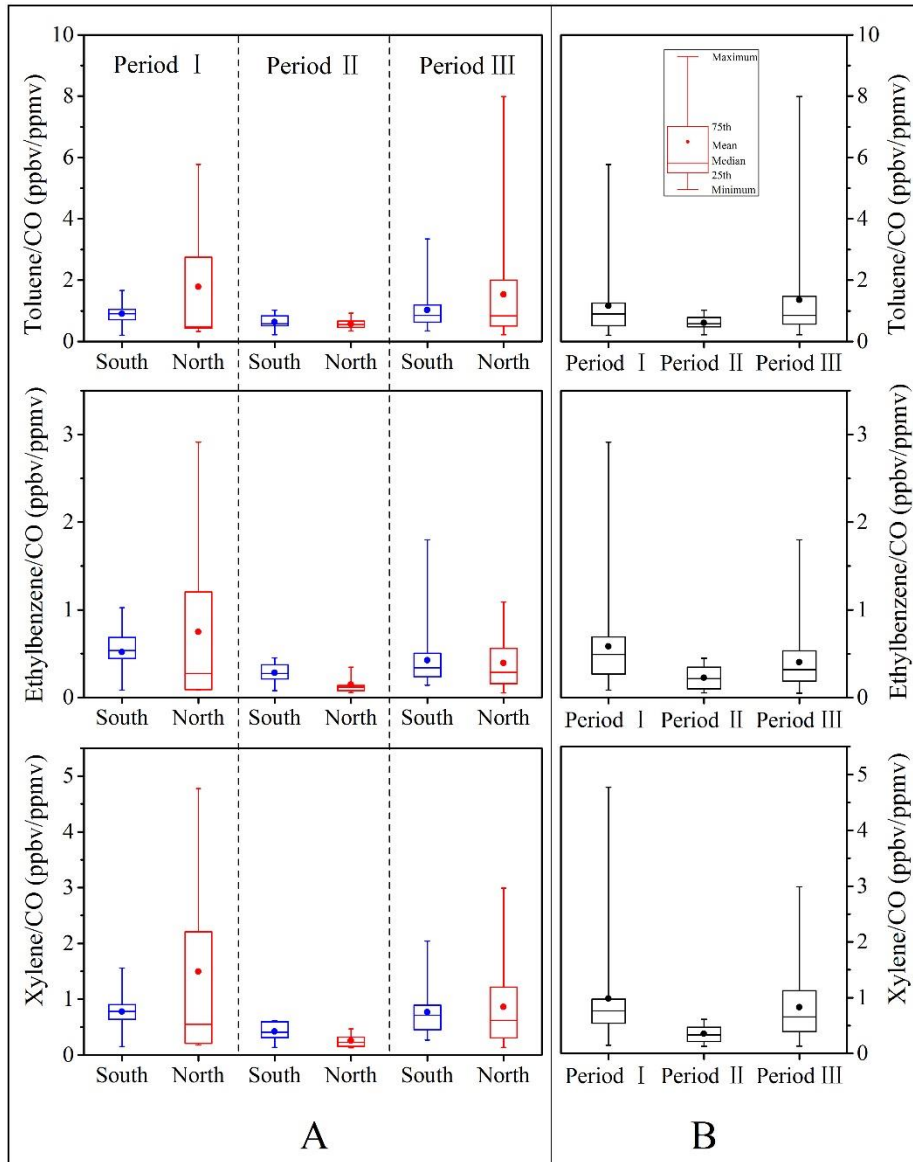
1068

1069 Figure 5. Ratios of aromatic hydrocarbons to carbon monoxide (CO) (A) in the air

1070 masses from the south and north regions and (B) in all samples during period I, II and

1071 III. (The lower and upper boundaries of the box represent the 25th and 75th

1072 percentiles, respectively; the whiskers below and above the box indicate the minimum

1073 and maximum, respectively; the line within the box marks the median; the dot
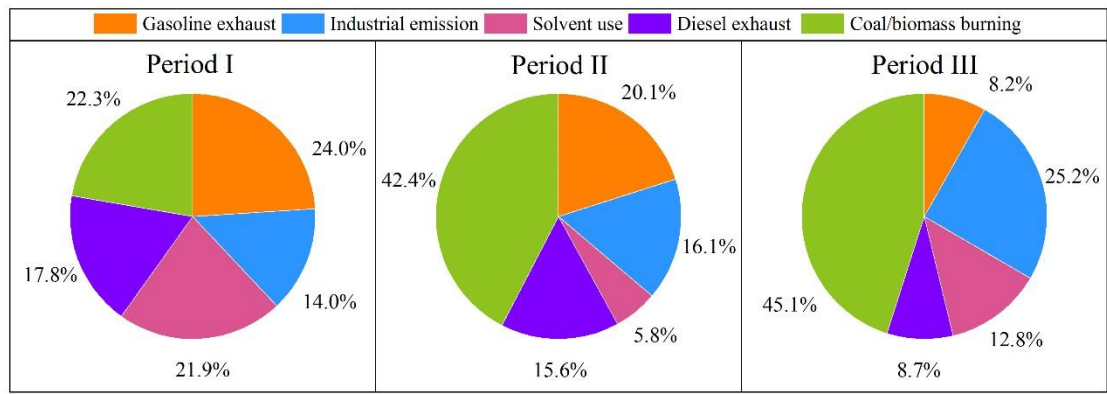
1074 represent the mean).

1075
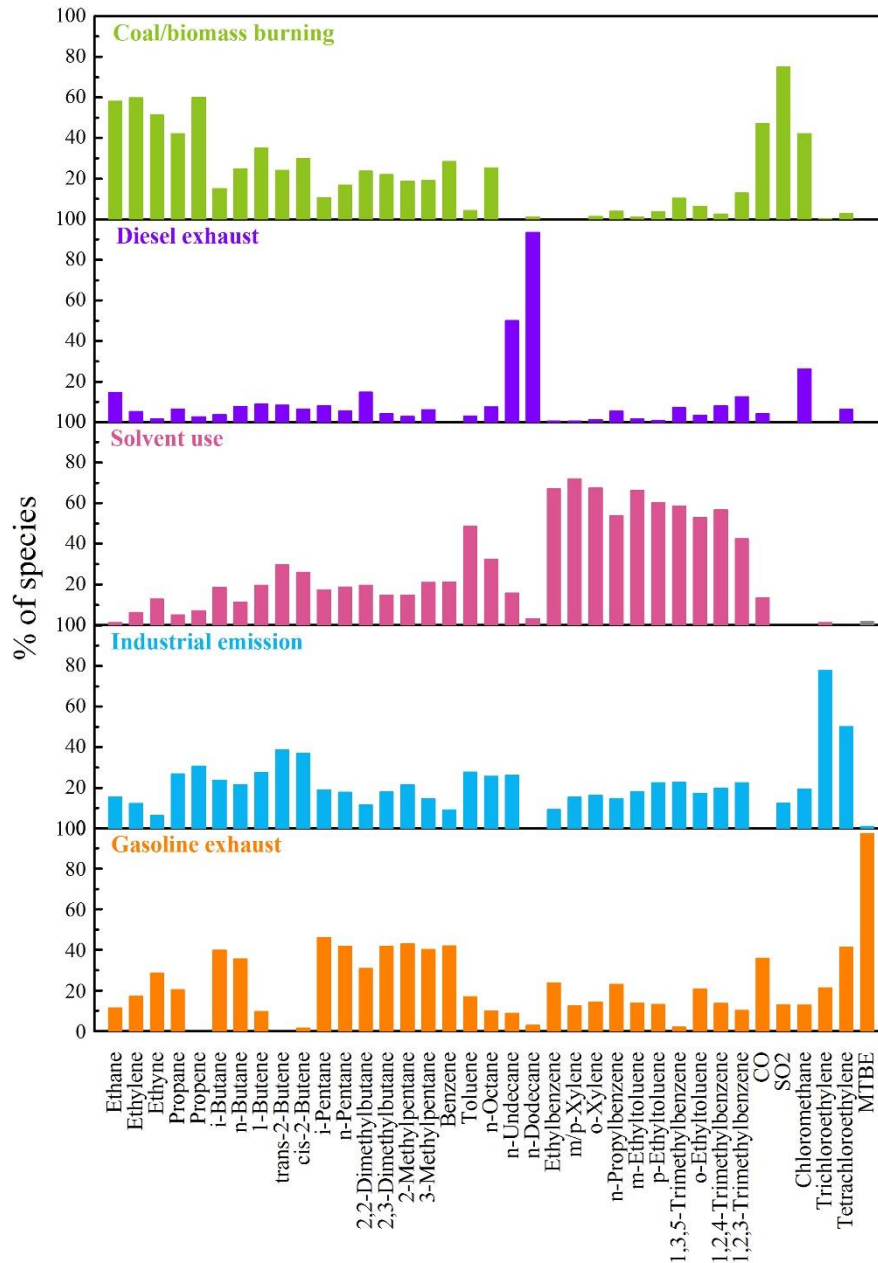
Figure 6. Source profiles revolved by PMF.

Figure 7. Contributions to VOCs in percentages (%) by different sources during period I, II and III.
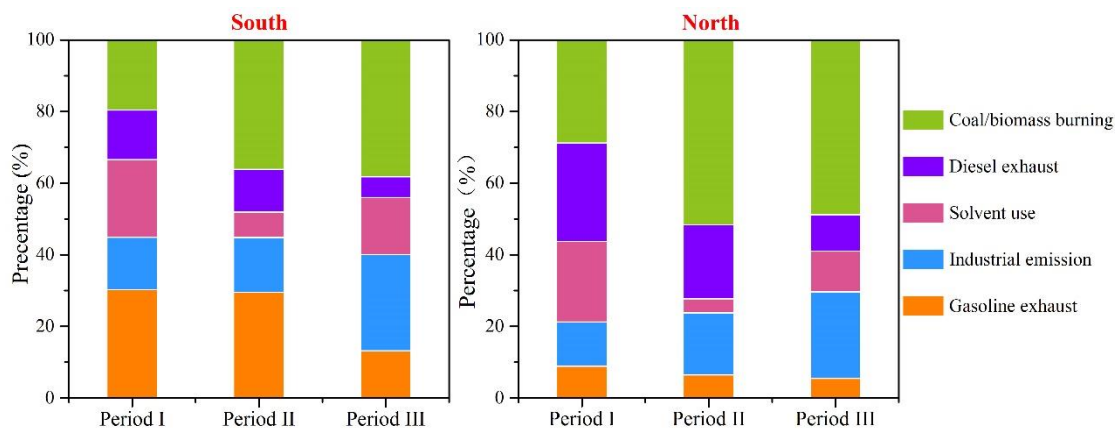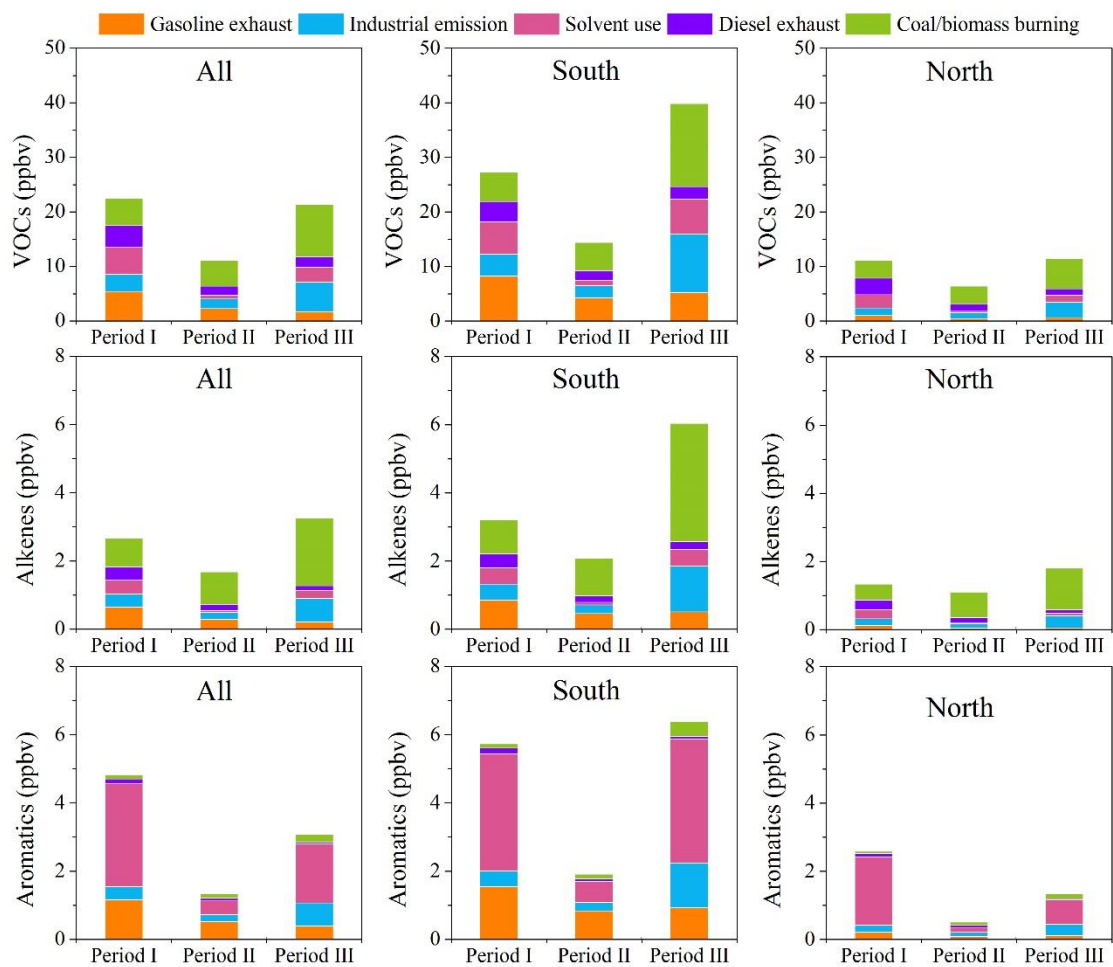
Figure 8. Sources contributions (%) to VOCs in the air masses from the south and north regions during period I, II and III.
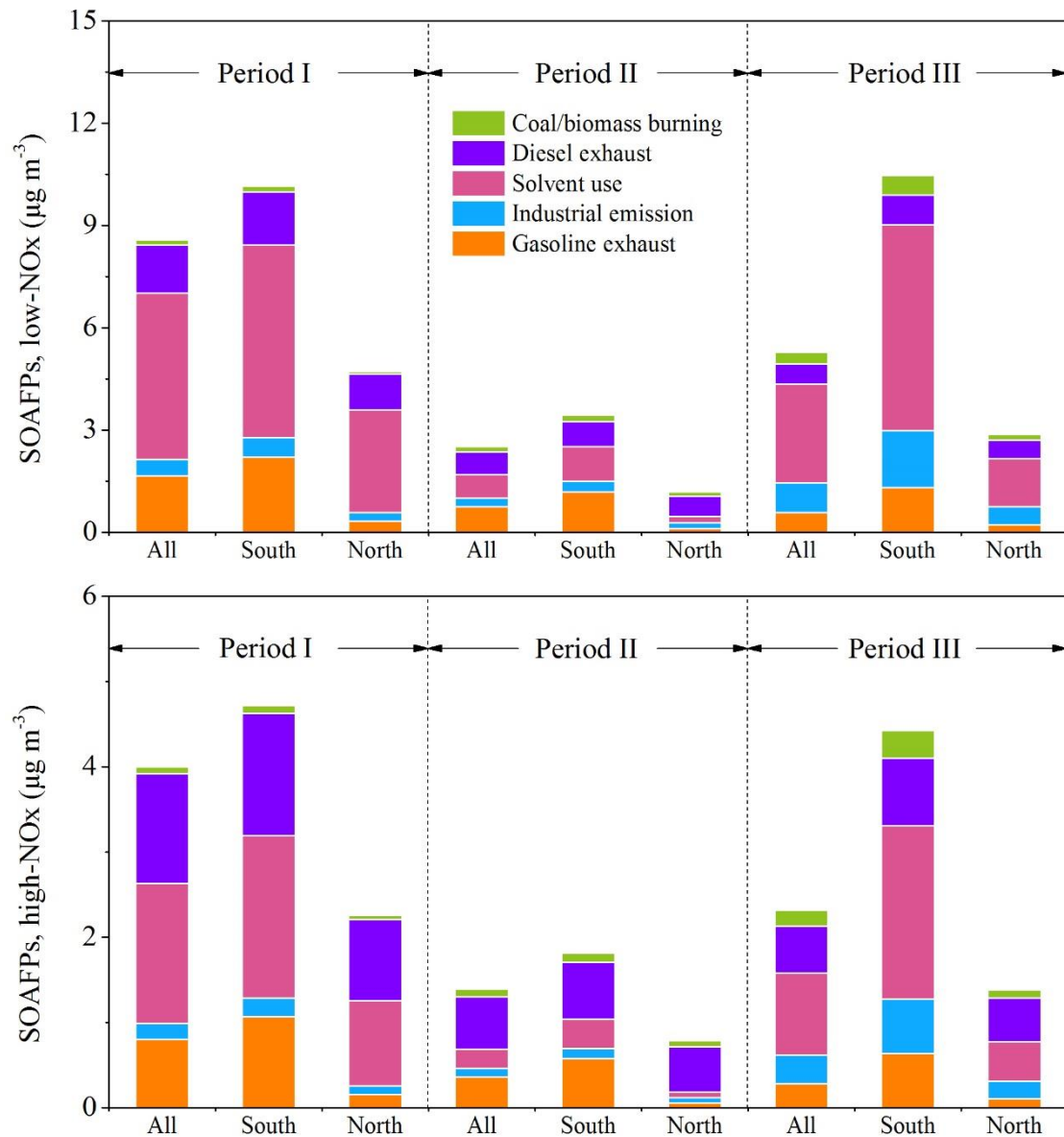
1087

Figure 9. Sources contributions of VOCs and reactive alkenes and aromatics in all samples and in air masses from the south and north regions during period I, II and III.

1090

Figure 10. Contributions to SOAFPs by different sources in the air masses from the south and north regions during period I, II and III.