

1 **Characterization of ambient volatile organic compounds**  
2 **and their sources in Beijing, before, during, and after**  
3 **Asia-Pacific Economic Cooperation China 2014**

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5 **J. Li, S. D. Xie\*, L. M. Zeng, L. Y. Li, Y. Q. Li and R. R. Wu**

6 College of Environmental Science and Engineering, State Key Joint Laboratory of  
7 Environmental Simulation and Pollution Control, Peking University,  
8 Beijing, People's Republic of China

9 \*Correspondence to: S. D. Xie (sdxie@pku.edu.cn)

10 **Abstract.**

11 Ambient volatile organic compounds (VOCs) were measured using an online system, gas  
12 chromatography-mass spectrometry/flame ionization detector (GC-MS/FID), in Beijing, China,  
13 before, during and after Asia-Pacific Economic Cooperation (APEC) China 2014, when  
14 stringent air quality control measures were implemented. Positive matrix factorization (PMF)  
15 was applied to identify the major VOC contributing sources and their temporal variations. The  
16 secondary organic aerosols potential (SOAP) approach was used to estimate variations of  
17 precursor source contributions to SOA formation. The average VOC mixing ratios during the  
18 three periods were 86.17, 48.28, and 72.97 ppbv, respectively. The mixing ratios of total VOC  
19 during the control period were reduced by 44%, and the mixing ratios of acetonitrile,  
20 halocarbons, oxygenated VOCs (OVOCs), aromatics, acetylene, alkanes and alkenes decreased  
21 by approximately 65%, 62%, 54%, 53%, 37%, 36%, and 23%, respectively. The mixing ratios  
22 of all measured VOC species decreased during control, and the most affected species were  
23 chlorinated VOCs (chloroethane, 1,1-dichloroethylene, chlorobenzene). PMF analysis  
24 indicated eight major sources of ambient VOCs, and emissions from target control sources were  
25 clearly reduced during the control period. Compared with the values before control,  
26 contributions of vehicular exhaust were most reduced, followed by industrial manufacturing  
27 and solvent utilization. Reductions of these three sources were responsible for 50%, 26%, and  
28 16% of the reductions in ambient VOCs. Contributions of evaporated or liquid gasoline and  
29 industrial chemical feedstock were slightly reduced, and contributions of secondary and long-

30 lived species were relatively stable. Due to central heating, emissions from fuel combustion  
31 kept on increasing during the whole campaign; because of weak control of liquid petroleum gas  
32 (LPG), the highest emissions of LPG occurred in the control period. Vehicle-related sources  
33 were the most important precursor sources likely responsible for the reduction in SOA  
34 formation during this campaign.

35

## 36 **1 Introduction**

37 Beijing, the capital of China, is one of the megacities in the world, with a population of more  
38 than 20 million and a vehicle fleet of more than 5 million (Beijing Statistical Yearbook, 2014).  
39 High levels of coal consumption, thousands of active construction sites, and rapid increases in  
40 vehicles have resulted in high emissions of fine particles (PM<sub>2.5</sub>), sulfur dioxides (SO<sub>2</sub>),  
41 nitrogen oxides (NO<sub>x</sub>), and volatile organic compounds (VOCs) in Beijing (Tang et al., 2009;  
42 Han et al., 2013; Wang et al., 2014a).

43 In November 2014, China hosted the Asia-Pacific Economic Cooperation (APEC) Meeting  
44 in Beijing, including the Concluding Senior Officials' Meeting on 5–6 November, the 26th  
45 APEC Ministerial Meeting on 7–8 November, and the 22nd APEC Economic Leaders'  
46 Meeting on 10–11 November. As the host city, Beijing has set rigorous plans to reduce  
47 emissions of air pollutants in Beijing and neighboring regions from 1 to 12 November 2014,  
48 resulting in a period of air quality control. The target sources included vehicles, paint and  
49 solvent use, steel factories, chemical factories, power plants, etc. A detailed description of the  
50 control measures is provided in Table S1. As a result, air quality was greatly improved, and the  
51 phrase "APEC blue" was coined on social media to describe the clear sky. The city's daily PM<sub>2.5</sub>  
52 concentration during the control period fell to 43  $\mu\text{g m}^{-3}$ , a 55% reduction compared with the  
53 same dates the prior year, and daily average levels of SO<sub>2</sub>, nitrogen dioxide (NO<sub>2</sub>), and PM<sub>10</sub>  
54 (aerosol particles with an aerodynamic diameter of less than 10  $\mu\text{m}$ ) decreased by 57%, 31%  
55 and 44%, respectively (Beijing Municipal Environmental Protection Bureau,  
56 <http://www.bjepb.gov.cn/>). However, sufficiently detailed information of ambient VOC mixing  
57 ratios and chemical compositions, as well as variations in their sources before, during, and after  
58 the control period has not been reported.

59 Many VOCs adversely affect public health (The Clean Air Act Amendments of 1990,  
60 [http://www.epa.gov/oar/caa/caaa\\_overview.html](http://www.epa.gov/oar/caa/caaa_overview.html)), and high levels of ambient VOCs have been  
61 detected in Beijing, likely associated with rapid economic development. For example, during

62 1980–2005, VOC emissions increased at an annual average rate of 10.6% in Beijing (Bo et al.,  
63 2008). Ambient VOC measurements during 2002–2003 at six sites in Beijing revealed an  
64 average total VOC concentration of  $132.6 \pm 52.2 \mu\text{g m}^{-3}$  with contributions from alkanes (35%),  
65 alkenes (17%), and aromatics (22%; Liu et al., 2005). A recent study has shown that non-  
66 methane hydrocarbon (NMHC) concentrations in Beijing are more than twice as high as in  
67 other cities (Wang et al., 2014b). Therefore, it is very necessary to formulate a cost-effective  
68 policy for reducing VOC emissions in Beijing.

69 VOCs play an important role in the formation of secondary organic aerosol (SOA) (Johnson  
70 et al., 2006; Ran et al., 2011; Zhang et al., 2014).  $\text{PM}_{2.5}$  is a key air pollutant in terms of adverse  
71 human health effects and visibility degradation (Tao et al., 2014). The severe haze pollution in  
72 Beijing was driven to a large extent by secondary aerosol formation, which contributed 30%–  
73 77% and 44%–71% of  $\text{PM}_{2.5}$  and of organic aerosol concentrations, respectively (Huang et al.,  
74 2014). Detailed information on VOC characteristics before, during, and after the control period  
75 will help future study on SOA formation mechanisms. Assessing VOC source variations will  
76 be essential to understanding the effect of abatement measures for VOCs and SOA formation.

77 To quantitatively assess the contributions of different sources to ambient VOC levels, we  
78 can use a combination of direct VOC measurements and receptor models. Receptor models are  
79 statistical tools used to identify and quantify sources of ambient air pollution at a given location  
80 by analyzing concentration data obtained at a receptor site without emission inventories. Source  
81 apportionment tools such as principal component analysis, Unmix, chemical mass balance, and  
82 positive matrix factorization (PMF) have been previously developed (Paatero et al., 1994;  
83 Watson et al., 2001). The latter is widely used to study VOC source contributions in urban areas  
84 because only time series of observed concentrations are used for the input parameters of the  
85 PMF calculation, which means that PMF results are not affected by uncertainties in emission  
86 profiles (Bon et al., 2011; McCarthy et al., 2013). With PMF, it is also possible to calculate  
87 contributions from unknown emission sources. The concept of secondary organic aerosol  
88 potential (SOAP) has been developed to reflect the propensity of each organic compound to  
89 form SOA on the basis of an equal mass emitted relative to toluene (Derwent et al., 1998;  
90 Derwent et al., 2010). By combining the SOAP scale with contributions from different sources  
91 to ambient VOC levels, it has been possible to evaluate the effect of abatement measures for  
92 SOA formation.

93 In this study, we measured 102 VOC species using online instruments at an observatory at  
94 Peking University in 2014, from 18 October to 22 November. The hourly mixing ratios and  
95 chemical compositions of ambient VOCs before, during and after the control period were  
96 investigated. A PMF model was used to extract the VOC sources for this campaign, and  
97 comparison of the source contributions before, during and after the control period help to  
98 evaluate the effect of the control measures on VOCs. SOAP-weighted mass contributions of  
99 each VOC source were used to estimate variations of precursor source contributions to SOA  
100 formation.

101

## 102 **2 Methodology**

### 103 **2.1 Sampling site**

104 We sampled on the roof of the technical physics building at Peking University (PKU) (39.99°  
105 N, 116.33° E), ~20 m above ground. PKU is located in a primarily residential and commercial  
106 area in northwestern Beijing (Fig. 1). Local VOC emission sources within 1 km of PKU include  
107 vehicular traffic and fuel combustion for cooking; additionally, a fourth ring road that carries  
108 very heavy traffic is located directly south of the site.

109 Samples were collected at an interval of 1 h from 18 October to 22 November, 2014. To  
110 determine the effect of the control plans, we divided the whole study into three parts: before  
111 APEC China 2014 (18–31 October), during APEC China 2014 (control period; 3– 12  
112 November.) and after APEC China 2014 (13–22 November). We did not use samples collected  
113 on 1 or 2 November because they represented a transition from the non-source control to the  
114 control period. The average temperatures before, during, and after the control period were  
115 12.63 °C, 7.37 °C, and 5 °C, respectively. The average wind speeds were 3.86, 6.85, and 5 m s<sup>-1</sup>,  
116 respectively. Meteorological data were collected from the NOAA Satellite and Information  
117 Service (<http://www7.ncdc.noaa.gov/CDO/cdo>).

### 118 **2.2 Sampling and analysis**

119 Ambient VOCs were collected and analyzed continuously and automatically using a custom-  
120 built online system, GC-MS/FID, with a time resolution of 1 h (TH-PKU 300B, Yuan et al.,  
121 2012b; Li et al., 2014). The online system combines a sampling system, electronic refrigeration

122 technology, and GC-MS/FID to sample, pre-concentrate, and analyze VOC samples. Moisture  
123 and CO<sub>2</sub> are removed before VOC analysis. The system uses dual columns and dual detectors  
124 to simultaneously analyze C<sub>2</sub>–C<sub>12</sub> VOCs, and the VOC species measured by GC-MS/FID are  
125 listed in Table S2. Most C<sub>2</sub>-C<sub>5</sub> hydrocarbons were separated on a PLOT-Al<sub>2</sub>O<sub>3</sub> column  
126 (15m×0.32mm ID×3μm, J&W Scientific, USA), and measured by the FID channel. Other  
127 compounds were separated on a semi-polar column (DB-624, 60m×0.25mm ID×1.4μm, J&W  
128 Scientific, USA) and quantified using a quadrupole MS detector.

129 These chemical analyses were subjected to rigorous quality assurance and quality control  
130 procedures. We used an external standard method for the quantification of C<sub>2</sub>–C<sub>5</sub> hydrocarbons,  
131 and an internal standard method for MS quantification of VOCs. Four compounds were used  
132 as internal standards: bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d<sub>5</sub>, and  
133 bromofluorobenzene. We used two sets of certificated standards, a mixture of 55 NMHCs  
134 (provided by the Environmental Technology Center, Canada), and a mixture of oxygenated  
135 VOCs (OVOCs) and halocarbons (provided by Linde Electronics and Specialty Gases, USA).  
136 Five concentrations (0.4–8 ppbv) were used to perform both calibrations. R<sup>2</sup> values for  
137 calibration curves were all above 0.999 and 0.99 for NMHCs and other species, respectively,  
138 indicating that integral areas of peaks were proportional to concentrations of target compounds.  
139 We performed daily calibrations, and the variations in target species responses were within ±  
140 10% of the calibration curve. The definitions of the method detection limit (MDL) for each  
141 compound are given in US Environmental Protection Agency (U.S. EPA) document TO-15,  
142 and the MDL of the online GC-MS/FID system for each species ranged from 0.002 to 0.070  
143 ppbv (Yuan et al., 2012). Detailed information of this system can be found in Li et al. (2014).

### 144 **2.3 Source apportionment**

145 The US PMF 5.0 (U.S.EPA, 2014) was applied to identify major VOC sources and their  
146 temporal variations. PMF assumes that measured concentrations at receptor sites are linear  
147 combinations of contributions from different factors (Paatero et al., 1994). Based on the  
148 uncertainties inherent in each observation, the PMF solution minimizes the objective function  
149  $Q$ , as shown in Eq. (1):

$$150 \quad Q = \sum_{i=1}^m \sum_{j=1}^n \left[ \frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2, \quad (1)$$

151 where  $u$  is the uncertainty estimate of source  $j$ , measured in sample  $i$ .

152 The detailed calculation method of uncertainty is shown in Reff et al. (2007). The best PMF  
153 solution should make the value of  $Q$  identical to that of  $Q_{theoretical}$ .  $Q_{theoretical}$  can be calculated  
154 as Eq. (2):

$$155 \quad Q_{theoretical} = i \times j - p \times (i + j), \quad (2)$$

156 where  $i$  is the number of samples,  $j$  is the number of species, and  $p$  is the number of factors.

157 There is a rotational ambiguity in PMF results, and one way to choose among possible  
158 solutions is to use the  $F_{peak}$  parameter. " $F_{peak}$ " is used to rotate an incorrect solution back to the  
159 real solution. The U.S.EPA PMF 5.0 has added two key components to the 3.0 version: two  
160 additional error estimation methods and source contribution constraints (Norris et al., 2014).

## 161 **2.4 Calculation of SOAP-weighted mass contributions of each VOC source**

162 SOAP-weighted mass contributions of each VOC source were used to estimate variations of  
163 precursor source contributions to SOA formation. The SOAP represents the propensity for an  
164 organic compound to form SOA when an additional mass emission of that compound is added  
165 to the ambient atmosphere expressed relative to that SOA formed when the same mass of  
166 toluene is added (Derwent et al., 2010). SOAPs are expressed as an index relative to toluene =  
167 100. Toluene was chosen as the basic compound for the SOAP scale because its emissions are  
168 well characterized and it is widely recognized as an important man-made precursor to SOA  
169 formation (Johnson et al., 2006b; Kleindienst et al., 2007; Hu et al., 2008). SOAPs, expressed  
170 relative to toluene=100, for 100 organic compounds are listed in Table S3, which are derived  
171 from Derwent et al. (2010).

172 We hypothesized that all measured VOC species would have the greatest effect on SOA  
173 formation. The SOAP-weighted mass contribution of each VOC source can be calculated using  
174 Eq. (3):

$$175 \quad SOAP_{weighted\ mass\ contribution} = \sum(VOCs)_{(i)} \times SOAP_{(i)} \quad (3)$$

176 where  $(VOCs)_{(i)}$  is the mass contribution of a VOC source to species  $i$  ( $\mu\text{g cm}^{-3}$ ), estimated by  
177 PMF analysis (linking with the molar mass of VOC species and basing on ideal gas law, we  
178 converts the unit of VOC species from ppbv to  $\mu\text{g m}^{-3}$ );  $SOAP_{(i)}$  is the SOA formation potential  
179 for species  $i$  (unitless, Table S3).

180 SOA formation is dependent on background environmental conditions, particularly  $\text{NO}_x$   
181 levels, which make it difficult to accurately quantify absolute SOA emissions. However,

182 because the SOAP approach references the SOA increments to toluene, it removes much of the  
183 influence of the uncertainties in the absolute SOA concentrations. Although SOAPs were  
184 obtained using highly idealized test conditions, this approach can be used to evaluate the  
185 relative contribution of each VOC source to the reduction of SOA during the air quality control  
186 period.

## 187 **3 Results and discussion**

### 188 **3.1 Mixing ratios and chemical speciation**

189 Ambient VOC mixing ratios and chemical compositions at PKU are summarized in Table 1.  
190 Before the control period, the mixing ratios of total VOCs averaged 86.17 ppbv and ranged  
191 from 17.05 to 247.93 ppbv. During control, this was reduced to 48.28 ppbv, with a range of  
192 9.39–147.95 ppbv. After the control period, the mixing ratios of total VOCs increased to an  
193 average of 72.97 ppbv. Thus, the mixing ratios of total VOCs were reduced by 43.97% during  
194 the control period compared with the period before control. Compared with the period after  
195 control, the mixing ratios were 33.16% lower during control.

196 Alkanes were the most abundant VOC group in all three periods, comprising 37%, 42% and  
197 36%, respectively. Although lower, the contribution of alkenes increased over time, with this  
198 group comprising 11%, 15% and 20% of total VOCs before, during, and after the control period,  
199 respectively. Compared with the period before control, the mixing ratios of alkanes, alkenes,  
200 aromatics, acetylene, OVOCs, halocarbons and acetonitrile decreased by approximately 36%,  
201 23%, 53%, 37%, 54%, 62%, and 65%, respectively, during control (Fig. 2). Notably,  
202 acetonitrile, halocarbons, OVOCs and aromatics were reduced by more than 50%. After the  
203 control period, alkanes and acetylene increased to the greatest extent, and mixing ratios were  
204 twice as high as those during control. The mixing ratios of other VOC groups increased by ~30%  
205 after the control period.

206 As each source type has its own fingerprint, variations in chemical compositions differed  
207 (Wang et al., 2010a). The average mixing ratio of the 102 measured species are listed in Table  
208 2. Ethane, ethylene, acetylene, propane and acetone are the five most abundant species during  
209 all the three periods. Compared with the period before control, the mixing ratios of all species  
210 decreased (Table 3). Tracers of industrial sources decreased most, including some halocarbons  
211 and esters. 2,2-Dimethylbutane, a tracer of motor vehicle exhaust (Chang et al., 2004), was one  
212 of the top 20 most decreased species.

### 213 3.2 Temporal distribution of ambient VOCs

214 Figure 3 displays the time series of total VOCs together with meteorological parameters  
215 observed at the PKU site during this campaign. This clearly shows two major pollution episodes,  
216 characterized by significantly elevated VOC concentrations. The first occurred during 18–19  
217 October (before control) and the second during 19–20 November (after control). During the  
218 first episode, the highest VOC mixing ratios were recorded at midnight on 18 October, when  
219 wind speed was relatively low ( $\sim 2 \text{ ms}^{-1}$ ), and VOC levels sharply increased from  $\sim 80$  ppbv to  
220  $\sim 250$  ppbv within 12 h. During the second episode, the peak VOC mixing ratio was more than  
221 270 ppbv, when wind speed was an average of  $2 \text{ m s}^{-1}$ , and VOC levels rose gradually from  
222  $\sim 90$  ppbv to  $\sim 270$  ppbv, perhaps caused by the accumulation of pollutants. During the control  
223 period, no heavy pollution occurred, but we found episodes of light pollution with elevated  
224 VOC mixing ratios: at midnight on 5 November and during the morning of 10 November. Both  
225 had peak values below 150 ppbv, significantly lower than those found before and after the  
226 control period.

227 To investigate pollution origins and transport pathways, 72-h air mass back trajectories  
228 arriving at an elevation of 100, 200, and 500 m were calculated at 12:00 am (16:00 UTC) on 19  
229 October and 4, 9, and 19 November for the PKU site using the NOAA Hybrid Single-Particle  
230 Lagrangian Integrated Trajectory (HYSPLIT) model (Fig. 4). This method showed that the air  
231 masses on 19 October originated from south China, and passed through Henan and Hebei  
232 Provinces, before reaching PKU (Fig. 4a). The air masses on 4 November originated from the  
233 northwest part of Inner Mongolia, and passed through Hebei Province, before reaching PKU  
234 (Fig. 4b). The air masses on 9 November originated from Mongolia and then passed through  
235 Inner Mongolia (Fig. 4c). The air mass on 19 November came from the south, passing through  
236 Shandong and Henan provinces (Fig. 4d).

237 The diurnal variations of ambient NMHCs and OVOCs before, during, and after the control  
238 period are shown in Fig. 5. NMHC values for the three periods showed similar daily variations:  
239 stable during the night, decreasing after sunrise, at a minimum in the afternoon (14:00–16:00  
240 LT), then increasing at night. This is likely caused by the descending boundary layer and  
241 possible night emissions (Li et al., 2014). In the control period, diurnal variations of NMHCs  
242 were less clear than those during the other periods, perhaps due to lower night emissions. There  
243 were no obvious daily variations in OVOCs. Because of secondary formation during the



244 daytime, photolysis loss, and variation in the boundary layer, ambient OVOC levels were stable  
245 (Chen et al., 2014).

246 During the period after control, nighttime NMHC mixing ratios were much higher than those  
247 before control, suggesting that nighttime emission sources may differ. We also found some  
248 evidence for the higher nighttime VOC mixing ratios in the period after control. Figure 6 shows  
249 the hourly average diurnal profiles for 2,2-dimethylbutane (2,2-DMB) and acetylene before,  
250 during, and after the control. 2,2-DMB is considered a typical tracer for vehicular emissions  
251 (Chang et al., 2004), and acetylene is a tracer for vehicular and other combustion processes  
252 (Baker et al., 2008). Before the control period, the highest-/lowest-value ratios (the highest  
253 average hourly mixing ratio of one VOC species divided by the lowest average hourly mixing  
254 ratio of this species) of acetylene and 2, 2-DMB were very similar with the values of 2.32 and  
255 2.13, respectively. During control, the highest-/lowest-value ratio of acetylene (3.05) became  
256 larger than the value of 2, 2-DMB (2.13). After control, the highest-/lowest-value ratio of  
257 acetylene (4.08) was significantly higher than the value of 2, 2-DMB (2.08). The highest-  
258 /lowest-value ratios of acetylene increased over time during the three periods, but the values of  
259 2, 2-DMB were relatively stable. So the influence from the planetary boundary layer and  
260 vehicular emissions on the higher nighttime mixing ratios of acetylene can be eliminated. Coal  
261 combustion was found to be an important source for ambient VOCs during winter in Beijing  
262 (Wang et al., 2013b). We speculate that combustion may have been an important nighttime  
263 source of VOCs during the second and the third periods.

### 264 **3.3 Variations of source emissions**

#### 265 **3.3.1 Identification of VOC sources**

266 Source apportionments were performed using a PMF model to calculate reductions in source  
267 emissions. We did not use species that were below MDL for more than 50% of the time or  
268 showed a significantly smaller signal to noise ratio (S/N). An S/N ratio was calculated for each  
269 species via PMF. After screening, 64 compounds, accounting for 90% of the total mixing ratios  
270 of the 102 VOC species, were used in the PMF analysis; the final data set comprised 695  
271 samples. Modeling was performed for 4–11 factors and the eight-factor solution was deemed  
272 to be most representative.

273 To attribute PMF factors to emission sources, we compared PMF profiles and reference  
274 profiles from the literature. Eight sources were identified: (1) LPG, (2) industrial manufacturing,

275 (3) industrial chemical feedstock, (4) fuel combustion, (5) solvent utilization, (6) evaporated or  
276 liquid gasoline, (7) vehicular exhaust, and (8) secondary and long-lived species. Modeled  
277 source profiles together with the relative contributions of individual sources to each analyzed  
278 species are shown in Fig. 7.

279 The first source shown in Fig. 7 is characterized by a significant amount of propane, i-butane,  
280 and n-butane, which are representative species in LPG samples in China (Lu et al., 2004). LPG  
281 is an important domestic cooking source in Beijing. In 2012, the annual use of LPG was  
282 ~391,200 to, of which 340,000 tons were used for cooking. Unlike in other large cities, LPG  
283 vehicle use is not widespread in Beijing, and the annual consumption of LPG in the transport  
284 sector in 2012 was only 3400 tons (China Energy Statistical Yearbooks, 2013). Therefore, this  
285 source likely represented emissions from residential LPG consumption, and was identified as  
286 “LPG”.

287 Both the second and third sources were industry-related. The second and third source profiles  
288 shown in Fig. 7 were characterized by high concentrations of chlorinated VOCs, which are  
289 tracers of industries (Scheff and Wadden, 1993; Jiun et al., 2008). The second source was also  
290 characterized by significant amounts of cyclopentane and methylmethacrylate. Cyclopentane is  
291 used in the manufacture of synthetic resins and rubber adhesives and as a blowing agent in the  
292 manufacture of polyurethane insulating foam; Methylmethacrylate is a transparent  
293 thermoplastic and often used as a lightweight or shatter-resistant alternative to soda-lime glass  
294 (Nagai et al., 2001). Therefore, this source was identified as “industrial manufacturing”. Key  
295 species of the third source profile include chloromethane, chloroform, n-hexane and acetone,  
296 all of which are widely used as feedstock in organic synthesis (U.S.EPA, 1994). The third  
297 source was identified as “industrial chemical feedstock”.

298 The fourth source profile shown in Fig. 7 was associated with over 50% of the total measured  
299 ethylene and acetylene mixing ratios, both of which were major species emitted from  
300 combustion process (Liu et al., 2008), and is therefore the believed to be from the combustion  
301 process. It was also characterized by significant amounts of ethane, propane, C3-C4 alkenes,  
302 and benzene. Ethane is a tracer of natural gas usage, and the source profiles of resident fuel  
303 combustion measured in China contained significant alkenes (Wang et al., 2013a). Moreira dos  
304 Santos et al. (2004) found that coal combustion can release significant amounts of benzene into  
305 the atmosphere. Therefore this source is believed to encompass combustion, and may include  
306 different fuel types, such as coal, straw and natural gas and was identified as “fuel combustion”.

307 The fifth source profile shown in Fig. 7 was rich in aromatic species (benzene, toluene,  
308 ethylbenzene, xylenes, BTEX) and esters (ethylacetate and n-butylacetate), and includes a  
309 certain amount of halocarbons (1,2-dichloroethane and 1,2-dichloropropane). BTEX is a major  
310 constituent of paints (Seila et al., 2001). Esters and halocarbons are used as industrial solvents  
311 or adhesives found in paint strippers, varnishes, and furniture (Cai et al., 2010). Thus, this  
312 source was considered to be a composite of emissions from solvent use and industrial coatings  
313 (Seila et al., 2001). Some major VOC emission sources—such as car manufacturing, printing,  
314 furniture manufacturing, shoe making and toy making—are mainly associated with painting  
315 and adhesive use and are included in this source category of “solvent utilization”.

316 Both the sixth and seventh source profiles included high mixing ratios of 2,2,4-  
317 trimethylpentane and MTBE. 2,2,4-Trimethylpentane is a fuel additive used to gain higher  
318 octane ratings (McCarthy et al., 2013). MTBE is a common gasoline additive in Beijing (Song  
319 et al., 2007). The two sources are both related to vehicle activities. The sources differ in ethane  
320 and acetylene mixing ratios, which are higher in the seventh source but are very low in the sixth  
321 source. Ethane and acetylene can be formed during the combustion process (Song et al., 2007),  
322 so the sixth factor may be an evaporated or liquid gasoline factor and source seven may be a  
323 mixture of evaporated or liquid gasoline and vehicular exhaust with rich BTEX, OVOCs, and  
324 heavy alkanes, which are tracers of gasoline and diesel exhaust (Liu et al., 2008). This was  
325 confirmed by a comparison with typical VOC ratios determined for vehicular exhaust. The  
326 mean toluene/benzene ratio of the seventh source profile was 1.50, and Jobson et al. (2004)  
327 observe a ratio of 1.59 for vehicular exhaust from several tunnel studies, thus it was identified  
328 as “vehicular exhaust”.

329 The eighth source profile, as shown in Fig. 7, is characterized by 52% of the total Freon113  
330 mixing ratios, 47% of the total 1,1,2,2-tetrachloroethane mixing ratios, and 41% of the total  
331 tetrachloromethane mixing ratios. These chemicals have a long lifespan in the atmosphere  
332 (McCarthy et al., 2007). The eighth source profile also consists of most carbonyls: acetone,  
333 propanal, n-pentanal, n-butanal and n-Hexanal. Considering the abundances of long lifetime  
334 compounds and carbonyls, we believe that the loadings of VOC species in this source were  
335 related to secondary formation and background levels. With a relatively constant contribution,  
336 this source was identified as “secondary and long-lived species”.

### 337 **3.3.2 Estimation of source contributions**

338 The hourly mixing ratio contributions of each VOC source are presented in Fig. 8. Compared  
339 with the non-control periods, the reconstructed mixing ratios of most sources were lower during  
340 the control period, including those of industrial manufacturing, industrial chemical feedstock,  
341 solvent utilization, evaporated or liquid gasoline, and vehicular exhaust. In contrast, the mixing  
342 ratio contributions of LPG showed higher values during the control period. The contributions  
343 of fuel combustion increased continuously over time, and the contributions of secondary and  
344 long-lived species were relatively constant.

345 Figure 9 illustrates source contribution percentages before, during and after control, and table  
346 4 lists the source mixing ratio contributions during the three periods. Before control, vehicular  
347 exhaust was the largest contributor (35%) to VOC mixing ratios, contributing 27.82 ppbv,  
348 followed by industrial manufacturing (13.51 ppbv, 17%) and solvent utilization (9.68 ppbv,  
349 12%). Fuel combustion, LPG, evaporated or liquid gasoline, secondary and long-lived species,  
350 and industrial chemical feedstock contributed 7.05, 6.21, 6.09, 4.47, and 4.01 ppbv, accounting  
351 for 9%, 8%, 8%, 6%, and 5% of the total VOC mixing ratios, respectively. The vehicle-related  
352 emission sources, (vehicle exhaust and evaporated or liquid gasoline) together accounted for  
353 43% of the VOC mixing ratios. The industrial-related emissions, (industrial manufacturing and  
354 chemical feedstock) together accounted for 22% of the VOC mixing ratios. This indicated that  
355 traffic and industry sources were major VOC sources before the control period.

356 During the control period, the largest contributor was fuel combustion, with 12.70 ppbv,  
357 accounting for 27% of total VOCs. The second largest contributor was vehicular exhaust, with  
358 8.17 ppbv, accounting for 17% of total VOCs. Contributions from LPG and secondary and  
359 long-lived species were 7.55 and 5.00 ppbv, respectively. Contributions from industrial  
360 chemical feedstock, solvent utilization and evaporated or liquid gasoline were 3.66, 3.48, and  
361 3.24 ppbv, accounting for 8%, 7%, and 7% of total VOCs, respectively. The contribution from  
362 industrial manufacturing was relatively low, at 3.22 ppbv.

363 After control, the city turns to the central heating period and the largest contributor was fuel  
364 combustion, with 31.77 ppbv, accounting for 45% of total VOCs. Vehicular exhaust, solvent  
365 utilization, industrial manufacturing, secondary and long-lived species, evaporated or liquid  
366 gasoline, industrial chemical feedstock and LPG contributed 9.98, 8.05, 6.10, 4.05, 3.72, 3.50,  
367 and 3.01 ppbv, accounting for 14%, 11%, 9%, 6%, 5%, 5%, and 4% of total VOCs, respectively.

368 Compared with the period before the control, the contributions of vehicular exhaust during the  
369 control were reduced to the greatest extent, with a value of 19.65 ppbv, followed by industrial  
370 manufacturing (10.29 ppbv) and solvent utilization (6.20 ppbv). Evaporated or liquid gasoline  
371 and industrial chemical feedstock were slightly reduced, with the values of 2.85 and 0.35 ppbv.  
372 Reductions of vehicular exhaust, industrial manufacturing, solvent utilization, evaporated or  
373 liquid gasoline, and industrial chemical feedstock were responsible for 50%, 26%, 16%, 7%,  
374 and 1% of the reductions in ambient VOCs, indicating that the control measures on traffic were  
375 most effective. The contributions of secondary and long-lived species were relatively stable. In  
376 contrast, due to central heating and weak control on fuel combustion and LPG, contributions  
377 from these sources were elevated by 80% and 22%, respectively. November is a transition  
378 month for central heating in northern China, which means that fuel combustion contributions  
379 would increase with time. Because of a lack of relative control measures for LPG, the peak  
380 contribution of this source occurred during the control period. The temperature difference  
381 during this campaign is relatively low, the influence from meteorological variability on VOC  
382 evaporation were not considered in this study.

### 383 **3.4 Precursor source contributions to SOA**

384 It is reported that during control the concentration of PM<sub>2.5</sub> reduced a lot (Beijing Municipal  
385 Environmental Protection Bureau, <http://www.bjepb.gov.cn/>). SOA constitute a significant  
386 fraction of PM<sub>2.5</sub> in China (Ding et al., 2012; Guo et al., 2012; Huang et al., 2014) and VOCs  
387 play an important role in the formation of SOA. The large reduction of VOCs may lead to the  
388 reduction of SOA and contribute to the PM<sub>2.5</sub> reduction. SOAP-weighted mass contributions of  
389 each VOC source were used to estimate the influence of variations of precursor emissions on  
390 SOA. The SOAP-weighted mass contributions of each VOC source before, during, and after  
391 the control period are listed in Table 5.

392 Before the control period, the SOAP-weighted mass contribution of vehicular-related sources  
393 was much higher than other VOC source with a value of 1613  $\mu\text{g cm}^{-3}$ , accounting for 43% of  
394 the total. In contrast, the SOAP-weighted mass contribution of each VOC source was very  
395 similar during the control period. Because of the abatement measures for pollutant emissions  
396 during the control period, the SOAP-weighted mass contributions of vehicular-related sources  
397 were most reduced compared with the period before control, with the value of 1013  $\mu\text{g cm}^{-3}$ ,  
398 explaining the 52% reduction in SOA.

399 Solvent utilization was the second largest source of man-made SOA precursors before  
400 control with the SOAP-weighted mass contributions of  $1132 \mu\text{g cm}^{-3}$ , accounting for 43% of  
401 the total. During the control period, the reduction in SOAP-weighted mass contributions from  
402 solvent utilization was  $725 \mu\text{g cm}^{-3}$ , explaining the 37% reduction in SOA. The reductions in  
403 other VOC sources were much smaller. Thus, vehicle and solvent utilization controls were the  
404 most important measures taken to reduce SOA during APEC Chain 2014 in Beijing.

405 Current knowledge about formation mechanisms of SOA is still very limited (Guo et al.,  
406 2012). We have to point out that the SOAP is computed to understand the potential to form  
407 SOA for VOC species, which cannot estimate the SOA formation from VOCs actually in certain  
408 atmospheric conditions. In this study, we used SOAP approach to discuss the effectiveness of  
409 the air quality controls. Detailed VOC data in this work will provide useful information for  
410 further study on the formation mechanisms of SOA.

#### 411 **4 Conclusions**

412 Mixing ratios of C<sub>2</sub>–C<sub>12</sub> VOCs were measured at an urban site in Beijing before, during and  
413 after the APEC China 2014. Total VOC mixing ratios were reduced by 44% during the control  
414 period, and the mixing ratios of acetonitrile, halocarbons, OVOCs, aromatics, acetylene,  
415 alkanes, and alkenes decreased by approximately 65%, 62 %, 54%, 53%, 37%, 36%, and 23%,  
416 respectively. The mixing ratios of all 102 measured species decreased, with that of chloroethane  
417 decreasing the most substantially. PMF analysis shows that contributions from controlled  
418 sources, i.e., vehicle-related sources, industrial manufacturing, and solvent utilization, were  
419 significantly reduced under air quality regulations. Among these, controls on vehicles were  
420 most effective, causing more than half of the reductions in ambient VOCs, and resulting in  
421 significant decreases in SOA. Industrial manufacturing controls were the second most  
422 important cause of ambient VOC reductions; control on solvent utilization appears to be the  
423 second important cause of SOA reductions. Fuel combustion was found to be an important  
424 source of ambient VOCs during the central heating period in Beijing.

425 Our results indicate that the stringent air quality restrictions implemented during APEC  
426 China 2014 were successful, and that controls on vehicles were the most important measures to  
427 ambient VOCs. As severe haze pollution events in China are mainly driven by secondary  
428 aerosol formation, these findings will also provide cost-effective solutions for lessening fine  
429 particle pollution. The detailed VOC provided here will provide information for further studies  
430 on the SOA formation and human health.

431

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436

437 **References**

- 438 Beijing Municipal Bureau of Statistics: Beijing Statistical Yearbook 2013[M], China Statistics  
439 Press, Beijing, 2014.
- 440 Baker, A. K., Beyersdorf, A. J., Doezema, L. A., Katzenstein, A., Meinardi, S., Simpson, I. J.,  
441 Blake, D. R., and Rowland, F. S.: Measurements of nonmethane hydrocarbons in 28 United  
442 States cities, *Atmos. Environ.*, 42, 170-182, 10.1016/j.atmosenv.2007.09.007, 2008.
- 443 Bo, Y., Cai, H., and Xie, S. D.: Spatial and temporal variation of historical anthropogenic  
444 NMVOCs emission inventories in China, *Atmos. Chem. Phys.*, 8, 7297-7316, 2008.
- 445 Bon, D. M., Ulbrich, I. M., de Gouw, J. A., Warneke, C., Kuster, W. C., Alexander, M. L.,  
446 Baker, A., Beyersdorf, A. J., Blake, D., Fall, R., Jimenez, J. L., Herndon, S. C., Huey, L. G.,  
447 Knighton, W. B., Ortega, J., Springston, S., and Vargas, O.: Measurements of volatile organic  
448 compounds at a suburban ground site (T1) in Mexico City during the MILAGRO 2006  
449 campaign: measurement comparison, emission ratios, and source attribution, *Atmos. Chem.*  
450 *Phys.*, 11, 2399-2421, 10.5194/acp-11-2399-2011, 2011.
- 451 Cai, C. J., Geng, F. H., Tie, X. X., Yu, Q. O., and An, J. L.: Characteristics and source  
452 apportionment of VOCs measured in Shanghai, China, *Atmos. Environ.*, 44, 5005-5014,  
453 10.1016/j.atmosenv.2010.07.059, 2010.
- 454 China National Bureau of Statistics: China Energy Statistical Yearbooks [M], China Statistics  
455 Press, Beijing, 2013.
- 456 Chang, C. C., Chen, T. Y., Chou, C., and Liu, S. C.: Assessment of traffic contribution to  
457 hydrocarbons using 2,2-dimethylbutane as a vehicular indicator, *Terr. Atmos. Ocean. Sci.*, 15,  
458 697-711, 2004.
- 459 Chen, W. T., Shao, M., Lu, S. H., Wang, M., Zeng, L. M., Yuan, B., and Liu, Y.: Understanding  
460 primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF  
461 model, *Atmos. Chem. Phys.*, 14, 3047-3062, 10.5194/acp-14-3047-2014, 2014.
- 462 Derwent, R. G., Jenkin, M. E., Utembe, S. R., Shallcross, D. E., Murrells, T. P., and Passant,  
463 N. R.: Secondary organic aerosol formation from a large number of reactive man-made organic  
464 compounds, *Sci. Total. Environ.*, 408, 3374-3381, 10.1016/j.scitotenv.2010.04.013, 2010.



465 Ding X, Wang X M, Gao B, et al. Tracer-based estimation of secondary organic carbon in the  
466 Pearl River Delta, south China [J]. *J. Geophys. Res.-Atmos.*, 2012,117,  
467 D05313,doi:10.1029/2011JD016596.

468 Gary Norris: EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, U.S.,  
469 2014

470 Guo, S., Hu, M., Guo, Q., Zhang, X., Zheng, M., Zheng, J., Chang, C. C., Schauer, J. J., and  
471 Zhang, R.: Primary Sources and Secondary Formation of Organic Aerosols in Beijing, China,  
472 *Environ. Sci. Technol.*, 46, 9846-9853, 10.1021/es20425641, 2012.

473 Han, X., Zhang, M. G., Tao, J. H., Wang, L. L., Gao, J., Wang, S. L., and Chai, F. H.: Modeling  
474 aerosol impacts on atmospheric visibility in Beijing with RAMS-CMAQ, *Atmos. Environ.*, 72,  
475 177-191, 10.1016/j.atmosenv.2013.02.030, 2013.

476 Hu, D., Bian, Q., Li, T. W. Y., Lau, A. K. H., and Yu, J. Z.: Contributions of isoprene,  
477 monoterpenes, beta-caryophyllene, and toluene to secondary organic aerosols in Hong Kong  
478 during the summer of 2006, *J. Geophys. Res.-Atmos.*, 113, 10.1029/2008jd010437, 2008.

479 Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R.,  
480 Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Brun, E. A., Crippa,  
481 M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J.,  
482 Zimmermann, R., An, Z. S., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S. H.:  
483 High secondary aerosol contribution to particulate pollution during haze events in China,  
484 *Nature*, 514, 218-222, 10.1038/nature13774, 2014.

485 Jiun-Horng, T., Kuo-Hsiung, L., Chih-Yu, C., Nina, L., Sen-Yi, M., and Hung-Lung, C.:  
486 Volatile organic compound constituents from an integrated iron and steel facility, *J. Health*  
487 *Econ.*, 157, 569-578, 10.1016/j.jhazmat.2008.01.022, 2008.

488 Johnson, D., Utembe, S. R., and Jenkin, M. E.: Simulating the detailed chemical composition  
489 of secondary organic aerosol formed on a regional scale during the TORCH 2003 campaign in  
490 the southern UK, *Atmos. Chem. Phys.*, 6, 419-431, 2006.

491 Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V.,  
492 and Edney, E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons  
493 to secondary organic aerosol at a southeastern US location, *Atmos. Environ.*, 41, 8288-8300,  
494 10.1016/j.atmosenv.2007.06.045, 2007.

495 Kuster, W. C., Jobson, B. T., Karl, T., Riemer, D., Apel, E., Goldan, P. D., and Fehsenfeld, F.  
496 C.: Intercomparison of volatile organic carbon measurement techniques and data at la porte  
497 during the TexAQS2000 Air Quality Study, *Environ. Sci. Technol.*, 38, 221-228,  
498 10.1021/es034710r, 2004.

499 Li, L. Y., Chen, Y., Zeng, L. M., Shao, M., Xie, S. D., Chen, W. T., Lu, S. H., Wu, Y. S., and  
500 Cao, W.: Biomass burning contribution to ambient volatile organic compounds (VOCs) in the  
501 Chengdu-Chongqing Region (CCR), China, *Atmos. Environ.*, 99, 403-410,  
502 10.1016/j.atmosenv.2014.09.067, 2014.

503 Liu, Y., Shao, M., Fu, L. L., Lu, S. H., Zeng, L. M., and Tang, D. G.: Source profiles of volatile  
504 organic compounds (VOCs) measured in China: Part I, *Atmos. Environ.*, 42, 6247-6260,  
505 10.1016/j.atmosenv.2008.01.070, 2008.

506 Liu, Y., Shao, M., Zhang, J., Fu, L. L., and Lu, S. H.: Distributions and source apportionment  
507 of ambient volatile organic compounds in Beijing city, China, *J. Environ. Sci. Health Part A-*  
508 *Toxic/Hazard. Subst. Environ. Eng.*, 40, 1843-1860, 10.1080/10934520500182842, 2005.

509 Lu, S.H.: Source apportionment of anthropogenic emissions of volatileorganic compounds,  
510 MSc Thesis, Peking University, 2004.

511 McCarthy, M. C., Hafner, H. R., Chinkin, L. R., and Charrier, J. G.: Temporal variability of  
512 selected air toxics in the United States, *Atmos. Environ.*, 41, 7180-7194,  
513 10.1016/j.atmosenv.2007.05.037, 2007.

514 McCarthy, M. C., Aklilu, Y. A., Brown, S. G., and Lyder, D. A.: Source apportionment of  
515 volatile organic compounds measured in Edmonton, Alberta, *Atmos. Environ.*, 81, 504-516,  
516 10.1016/j.atmosenv.2013.09.016, 2013.

517 Nagai, K.: New developments in the production of methyl methacrylate, *Appl. Catal. A-Gen.*,  
518 221, 367-377, doi: 10.1016/s0926-860x (01)00810-9, 2001.

519 Norris, G., Duvall, R., Brown, S., and Song, B.: EPA positive matrix factorization (PMF) 5.0  
520 fundamentals and user guide, US Environmental Protection Agency, Office of Research and  
521 Development, Washington, DC, 2014.

522 Paatero, P.: User's guide for positive matrix factorization programs PMF2 and PMF3, Part 1:  
523 Tutorial, University of Helsinki, Helsinki, Finland, 2004.

524 Paatero, P., and Tapper, U.: Positive matrix factorization a nonnegative factor model with  
525 optimal utilization of error estimates of data values, *Environmetrics*, 5, 111-126,  
526 10.1002/env.3170050203, 1994.

527 Polissar, A. V., Hopke, P. K., and Paatero, P.: Atmospheric aerosol over Alaska - 2. Elemental  
528 composition and sources, *J. Geophys. Res.-Atmos.*, 103, 19045-19057, 10.1029/98jd01212,  
529 1998.

530 Ran, L., Zhao, C. S., Xu, W. Y., Lu, X. Q., Han, M., Lin, W. L., Yan, P., Xu, X. B., Deng, Z.  
531 Z., Ma, N., Liu, P. F., Yu, J., Liang, W. D., and Chen, L. L.: VOC reactivity and its effect on  
532 ozone production during the HaChi summer campaign, *Atmos. Chem. Phys.*, 11, 4657-4667,  
533 10.5194/acp-11-4657-2011, 2011.

534 Reff, A., Eberly, S. I., and Bhave, P. V.: Receptor modeling of ambient particulate matter data  
535 using positive matrix factorization: Review of existing methods, *J. Air. Waste. Manage.*, 57,  
536 146-154, 2007.

537 Santos, C. Y. M., Azevedo, D. D., and Aquino Neto, F. R.: Atmospheric distribution of organic  
538 compounds from urban areas near a coal-fired power station, *Atmos. Environ.*, 38, 1247-1257,  
539 10.1016/j.atmosenv.2003.11.026, 2004.

540 Scheff, P. A., and Wadden, R. A.: Receptor modeling of volatile organic compounds .1.  
541 Emission inventory and validation, *Environ. Sci. Technol.*, 27, 617-625, 10.1021/es00041a005,  
542 1993.

543 Schleicher, N., Norra, S., Chen, Y. Z., Chai, F. H., and Wang, S. L.: Efficiency of mitigation  
544 measures to reduce particulate air pollution-A case study during the Olympic Summer Games  
545 2008 in Beijing, China, *Sci. Total. Environ.*, 427, 146-158, 10.1016/j.scitotenv.2012.04.004,  
546 2012.

547 Seila, R. L., Main, H. H., Arriaga, J. L., Martinez, G., and Ramadan, A.: Atmospheric volatile  
548 organic compound measurements during the 1996 Paso del Norte Ozone Study, *Sci. Total.  
549 Environ.*, 276, 153-169, 10.1016/s0048-9697(01)00777-x, 2001.

550 Song, Y., Shao, M., Liu, Y., Lu, S. H., Kuster, W., Goldan, P., and Xie, S. D.: Source  
551 apportionment of ambient volatile organic compounds in Beijing, *Environ. Sci. Technol.*, 41,  
552 4348-4353, 10.1021/es0625982, 2007.

553 Tang, G., Li, X., Wang, Y., Xin, J., and Ren, X.: Surface ozone trend details and interpretations  
554 in Beijing, 2001-2006, *Atmos. Chem. Phys.*, 9, 8813-8823, 2009.

555 Tao, J., Gao, J., Zhang, L., Zhang, R., Che, H., Zhang, Z., Lin, Z., Jing, J., Cao, J., and Hsu, S.  
556 C.: PM<sub>2.5</sub> pollution in a megacity of southwest China: source apportionment and implication,  
557 *Atmos. Chem. Phys.*, 14, 8679-8699, 10.5194/acp-14-8679-2014, 2014.

558 U.S.EPA: Locating and Estimating Documents, Office of Air Quality Planning and Standards  
559 U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1994.

560 Wang, B., Shao, M., Lu, S. H., Yuan, B., Zhao, Y., Wang, M., Zhang, S. Q., and Wu, D.:  
561 Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008, *Atmos. Chem.*  
562 *Phys.*, 10, 5911-5923, 10.5194/acp-10-5911-2010, 2010a.

563 Wang, L. T., Xu, J., Yang, J., Zhao, X. J., Wei, W., Cheng, D. D., Pan, X. M., and Su, J.:  
564 Understanding haze pollution over the southern Hebei area of China using the CMAQ model,  
565 *Atmos. Environ.*, 56, 69-79, 10.1016/j.atmosenv.2012.04.013, 2012.

566 Wang, Q., Geng, C. M., Lu, S. H., Chen, W. T., and Shao, M.: Emission factors of gaseous  
567 carbonaceous species from residential combustion of coal and crop residue briquettes, *Front.*  
568 *Env. Sci. Eng.*, 7, 66-76, 10.1007/s11783-012-0428-5, 2013a.

569 Wang, M., Shao, M., Lu, S.-H., Yang, Y.-D., and Chen, W.-T.: Evidence of coal combustion  
570 contribution to ambient VOCs during winter in Beijing, *Chin. Chem. Lett.*, 24, 829-832,  
571 10.1016/j.ccllet.2013.05.029, 2013b.

572 Wang, M., Shao, M., Chen, W., Yuan, B., Lu, S., Zhang, Q., Zeng, L., and Wang, Q.: A  
573 temporally and spatially resolved validation of emission inventories by measurements of  
574 ambient volatile organic compounds in Beijing, China, *Atmos. Chem. Phys.*, 14, 5871-5891,  
575 10.5194/acp-14-5871-2014, 2014b.

576 Wang, Y. S., Yao, L., Wang, L. L., Liu, Z. R., Ji, D. S., Tang, G. Q., Zhang, J. K., Sun, Y., Hu,  
577 B., and Xin, J. Y.: Mechanism for the formation of the January 2013 heavy haze pollution  
578 episode over central and eastern China, *Sci. China-Earth Sci.*, 57, 14-25, 10.1007/s11430-013-  
579 4773-4, 2014a.

580 Watson, J. G., Chow, J. C., and Fujita, E. M.: Review of volatile organic compound source  
581 apportionment by chemical mass balance, *Atmos. Environ.*, 35, 1567-1584, 10.1016/s1352-  
582 2310(00)00461-1, 2001.

583 Wittig, A. E., and Allen, D. T.: Improvement of the Chemical Mass Balance model for  
584 apportioning - sources of non-methane hydrocarbons using composite aged source profiles,  
585 *Atmos. Environ.*, 42, 1319-1337, 10.1016/j.atmosenv.2007.10.072, 2008.

586 Yang, Q., Wang, Y. H., Zhao, C., Liu, Z., Gustafson, W. I., and Shao, M.: NO<sub>x</sub> Emission  
587 Reduction and its Effects on Ozone during the 2008 Olympic Games, *Environ. Sci. Technol.*,  
588 45, 6404-6410, 10.1021/es200675v, 2011.

589 Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S. H., Wang, M., Zeng, L. M., Zhang, Q.,  
590 Song, Y., Zhang, J. B., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How  
591 chemistry affects the interpretation of positive matrix factorization (PMF) analysis, *J. Geophys.*  
592 *Res.-Atmos.*, 117, 10.1029/2012jd018236, 2012.

593 Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.:  
594 VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern  
595 China, *Atmos. Chem. Phys.*, 13, 8815-8832, 10.5194/acp-13-8815-2013, 2013.

596 Zhang, Q., B. Yuan, M. Shao, X. Wang, S. Lu, K. Lu, M. Wang, L. Chen, C. C. Chang, and S.  
597 C. Liu (2014), Variations of ground-level O<sub>3</sub> and its precursors in Beijing in summertime  
598 between 2005 and 2011, *Atmos. Chem. Phys.*, 14(12), 6089-6101.

599 Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C. C.,  
600 and Liu, S. C.: Variations of ground-level O<sub>3</sub> and its precursors in Beijing in summertime  
601 between 2005 and 2011, *Atmos. Chem. Phys.*, 14, 6089-6101, 10.5194/acp-14-6089-2014,  
602 2014.

603

604 **Figure and Table captions:**

605 **Table 1.** Volatile organic compound (VOC) mixing ratios (ppbv), measured in Beijing.

606 **Table 2.** Average mixing ratios (ppbv) of volatile organic compound (VOC) species measured  
607 in Beijing.

608 **Table 3.** The top 20 volatile organic compound (VOC) species with the highest decreasing  
609 ratios.

610 **Table 4.** Source contributions (ppbv) derived by PMF analysis.

611 **Table 5.** SOAP-weighted mass contributions ( $\mu\text{g cm}^{-3}$ ) of each VOC source before, during,  
612 and after the control period during APEC China 2014.

613 **Figure 1.** The location of Beijing city in China and the sampling site in Beijing.

614 **Figure 2.** Mixing ratios of volatile organic compound (VOC) groups before, during, and after  
615 the control period during APEC China 2014.

616 **Figure 3.** Time series of total measured volatile organic compounds (VOCs), temperature, wind  
617 direction, and speed at PKU site during this study.

618 **Figure 4.** Three-day backward trajectories ending at 12:00 am (16:00 UTC) 19 October, 4, 9,  
619 and 19 November 2014.

620 **Figure 5.** Diurnal variations in mixing ratios of non-methane hydrocarbons (NMHCs) and  
621 oxygenated volatile organic compounds (OVOC) at the PKU site before, during, and after the  
622 control period during APEC China 2014.

623 **Figure 6.** Diurnal variations of mixing ratios of 2,2-dimethylbutane and acetylene at the PKU  
624 site before, during, and after the control period during APEC China 2014.

625 **Figure 7.** Eight source profiles (bars;  $\text{ppbv ppbv}^{-1}$ ) resolved from PMF model, and contribution  
626 percentages (dots) from each source factor.

627 **Figure 8.** Time series of hourly contributions from each identified source from 18 October to  
628 22 November 2014.

629 **Figure 9.** Over all contributions (%) for the eight sources identified by PMF analysis before,  
630 during, and after the control period during the APEC China 2014.

631 **Table 1.** Volatile organic compound (VOC) mixing ratios (ppbv), measured in Beijing.

VOC groups	Before(N <sup>a</sup> =240;17/10-31/10 <sup>b</sup> )		During(N=234;3/11-12/11)		After(N=221;13/11-22/11)	
	Rang	Average±sd	Rang	Average±sd	Rang	Average±sd
Alkanes	3.39-109.87	32.1±18.89	2.21-66.48	20.39±15.45	5.25-90.54	26.57±19.09
Alkenes	0.66-31.05	9.39±5.42	0.26-25.39	7.22±6.30	0.92-63.50	14.58±12.99
Aromatics	1.00-46.5	9.55±5.97	0.46-16.81	4.52±3.59	0.85-32.75	7.14±6.30
Acetylene	0.36-23.7	6.41±4.17	0.24-15.24	4.04±3.34	0.70-32.31	8.27±7.04
OVOCs	4.29-40.49	15.27±7.08	2.15-20.79	7.09±3.67	2.70-35.08	9.36±6.28
Halocarbons	4.71-34.14	12.37±5.28	1.89-14.33	4.64±2.35	1.84-46.89	6.54±5.85
Acetonitrile	0.20-19.71	1.09±2.37	0.08-4.35	0.38±0.40	0.11-1.50	0.49±0.33
Total VOCs	17.05-247.93	86.17±43.67	9.39-147.95	48.28±33.87	0.85-271.91	72.97±55.69

632 <sup>a</sup> Sampling number;

633 <sup>b</sup> Sampling date.

634

**Table 2.** Average mixing ratios (ppbv) of VOC species measured in Beijing.

Species	Before	During	After	Species	Before	During	After
Ethane	10.80	7.71	11.31	Trichloroethylene	0.14	0.07	0.08
Propane	6.38	4.44	5.40	1,2-Dichloropropane	1.01	0.36	0.67
Isobutane	2.32	1.57	1.75	Bromodichloromethane	0.00	0.00	0.00
n-Butane	3.27	1.89	2.25	trans-1,3-Dichloropropene	0.02	0.01	0.01
cyclopentane	0.35	0.09	0.14	cis-1,3-Dichloropropene	0.01	0.00	0.00
Isopentane	2.16	1.14	1.41	1,1,2-Trichloroethane	0.10	0.04	0.06
n-Pentane	1.61	0.74	0.99	Tetrachloroethylene	0.17	0.08	0.09
2,2-dimethylbutane	0.07	0.02	0.03	1,2-Dibromoethane	0.00	0.00	0.00
2,3-dimethylbutane	0.25	0.14	0.18	Chlorobenzene	0.05	0.01	0.02
2-methylpentane	0.73	0.44	0.54	Bromoform	0.00	0.00	0.00
3-methylpentane	0.49	0.25	0.27	1,1,2,2-Tetrachloroethane	0.23	0.14	0.14
n-hexane	0.93	0.66	0.62	1,3-Dichlorobenzene	0.00	0.00	0.00
2,4-dimethylpentane	0.06	0.03	0.03	1,4-Dichlorobenzene	0.09	0.08	0.08
methylcyclopentane	0.44	0.23	0.27	Benzylchloride	0.00	0.00	0.00
2-methylhexane	0.20	0.09	0.12	1,2-Dichlorobenzene	0.00	0.00	0.00
cyclohexane	0.41	0.13	0.18	acrolein	0.30	0.17	0.27
2,3-dimethylpentane	0.12	0.05	0.07	Propanal	0.61	0.30	0.31
3-methylhexane	0.21	0.10	0.14	Acetone	4.29	2.19	2.48
2,2,4-trimethylpentane	0.18	0.09	0.11	Methylacetate	1.02	0.39	0.56
n-heptane	0.26	0.12	0.18	MTBE	0.88	0.39	0.42
methylcyclohexane	0.23	0.08	0.12	Methacrolein	0.06	0.02	0.05
2,3,4-trimethylpentane	0.09	0.04	0.05	Vinylacetate	0.02	0.01	0.04
2-methylheptane	0.08	0.04	0.06	n-Butanal	0.15	0.07	0.08
3-methylheptane	0.05	0.02	0.03	Methylvinylketone	0.36	0.18	0.23
octane	0.13	0.07	0.10	Methylethylketone	1.79	0.59	0.76
n-nonane	0.10	0.05	0.08	Ethylacetate	2.12	0.88	1.39
n-decane	0.10	0.06	0.07	2-pentanone	0.07	0.03	0.04
Udecane	0.06	0.04	0.05	n-Pentanal	0.11	0.07	0.08
Dodecane	0.05	0.05	0.04	3-pentanone	0.02	0.01	0.01
Ethylene	7.18	5.51	11.23	Methylmethacrylate	1.73	0.97	1.37
Propene	1.33	1.16	2.42	n-Hexanal	0.46	0.25	0.28
trans-2-Butene	0.12	0.10	0.15	n-Butylacetate	1.28	0.57	1.00
1-Butene	0.35	0.22	0.42	Acetylene	6.41	4.04	8.27
cis-2-Butene	0.16	0.09	0.17	Acetonitrile	1.09	0.38	0.49
trans-2-pentene	0.06	0.03	0.05	benzene	1.98	1.02	1.87
isoprene	0.11	0.06	0.07	toluene	3.31	1.57	2.37
cis-2-pentene	0.03	0.01	0.02	ethylbenzene	1.13	0.49	0.74
1-hexene	0.05	0.03	0.05	m/p-xylene	1.01	0.48	0.71
Bromomethane	0.01	0.01	0.01	o-xylene	0.71	0.32	0.49
Chloroethane	0.10	0.02	0.04	styrene	0.24	0.11	0.21
Freon11(CFCl <sub>3</sub> )	3.61	0.58	0.85	isopropylbenzene	0.05	0.02	0.03
Freon113(C <sub>2</sub> F <sub>3</sub> Cl <sub>3</sub> )	0.09	0.08	0.08	n-propylbenzene	0.09	0.04	0.06
1,1-Dichloroethylene	0.01	0.00	0.00	3-ethyltoluene	0.25	0.10	0.16
Dichloromethane	3.76	2.00	2.60	4-ethyltoluene	0.13	0.05	0.08
1,1-Dichloroethane	0.26	0.11	0.15	1,3,5-trimethylbenzene	0.09	0.04	0.06
cis-1,2-Dichloroethylene	0.03	0.02	0.04	2-ethyltoluene	0.10	0.04	0.07
Chloroform	0.93	0.42	0.62	1,2,4-trimethylbenzene	0.29	0.13	0.19
1,1,1-Trichloroethane	0.01	0.00	0.00	1,2,3-trimethylbenzene	0.08	0.04	0.06
tetrachloromethane	0.16	0.11	0.12	1,3-diethylbenzene	0.02	0.01	0.01
1,2-Dichloroethane	1.58	0.49	0.87	1,4-diethylbenzene	0.06	0.04	0.04



636 **Table 3.** The top 20 volatile organic compound (VOC) species with the highest decreasing  
 637 ratios.

<b>Species</b>	<b>Decreasing ratio</b>	<b>Species</b>	<b>Decreasing ratio</b>
Chloroethane	80.34%	1,2-dichloropropane	64.27%
1,1-dichloroethylene	76.46%	Methylcyclohexane	63.67%
Chlorobenzene	74.24%	cis-1,3-dichloropropene	62.49%
Cyclopentane	72.58%	trans-1,3-dichloropropene	62.36%
1,2-dichloroethane	69.14%	Methylacetate	61.67%
Cyclohexane	68.13%	2,3-dimethylpentane	61.23%
Methylethylketone	66.91%	Ethylacetate	58.80%
Methacrolein	65.12%	4-ethyltoluene	58.39%
Acetonitrile	65.12%	3-ethyltoluene	58.25%
2,2-dimethylbutane	64.79%	1,1-dichloroethane	58.23%

638

639 **Table 4.** Source contributions (ppbv) derived by PMF analysis.

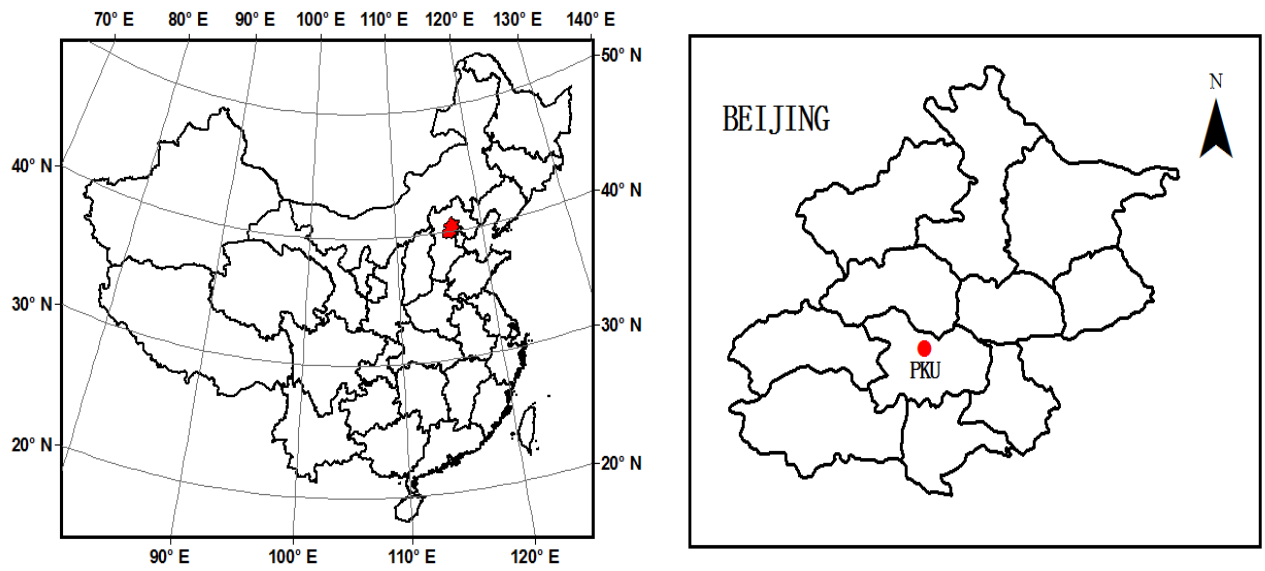
Source	Average source contribution		
	Before	During	After
LPG	6.21	7.55	3.01
Fuel combustion	7.05	12.70	31.77
Industrial manufacturing	13.51	3.22	6.10
Industrial chemical feedstock	4.01	3.66	3.50
Solvent utilization	9.68	3.48	8.05
Evaporated or liquid gasoline	6.09	3.24	3.72
Vehicular exhaust	27.82	8.17	9.98
Secondary and long-lived species	4.47	5.00	4.05
Total	78.85	47.02	70.18

640

641 **Table 5.** SOAP-weighted mass contributions ( $\mu\text{g cm}^{-3}$ ) of each VOC source before, during, and  
 642 after the control period during APEC China 2014.

Source	Source contribution		
	Before	During	After
LPG	143	174	69
Fuel combustion	158	285	711
Industrial manufacturing	494	118	223
Industrial Chemical feedstock	131	120	114
Solvent utilization	1132	407	941
Evaporated or liquid gasoline	526	280	321
Vehicular exhaust	1087	320	390
Secondary and long-lived species	89	99	80

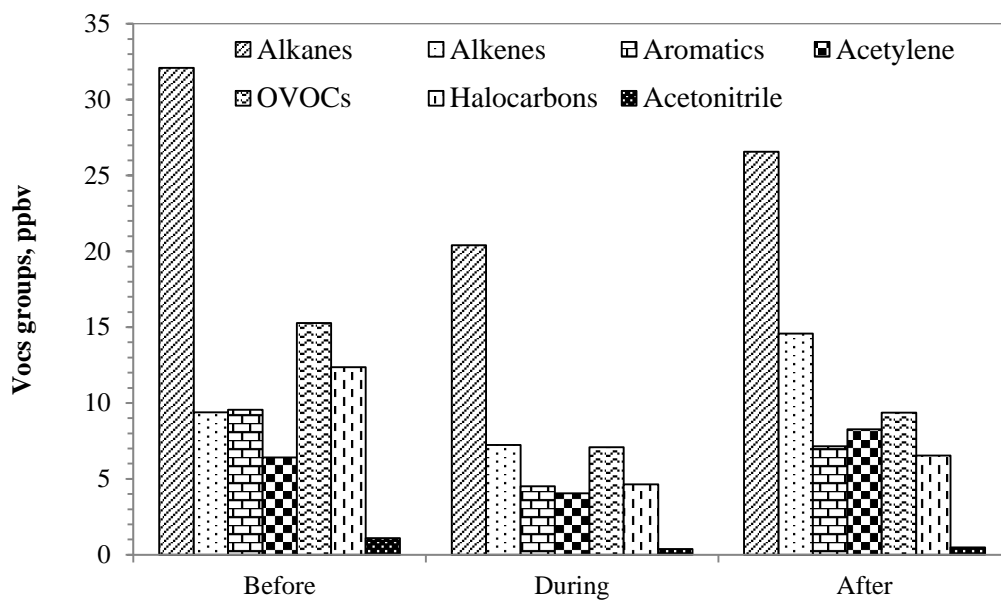
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644

645 **Figure 1.** The location of Beijing in China and the sampling site in Beijing.

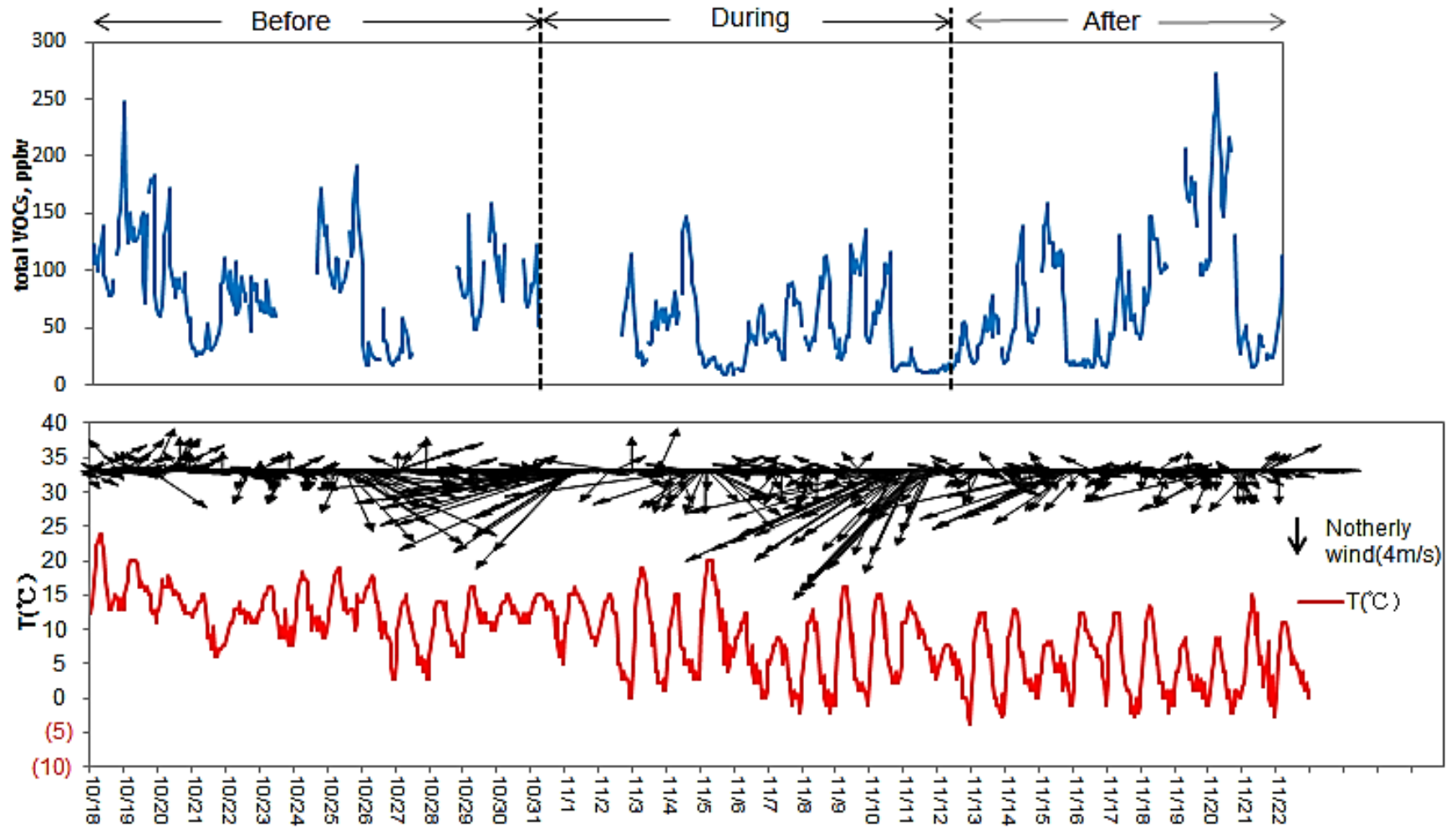
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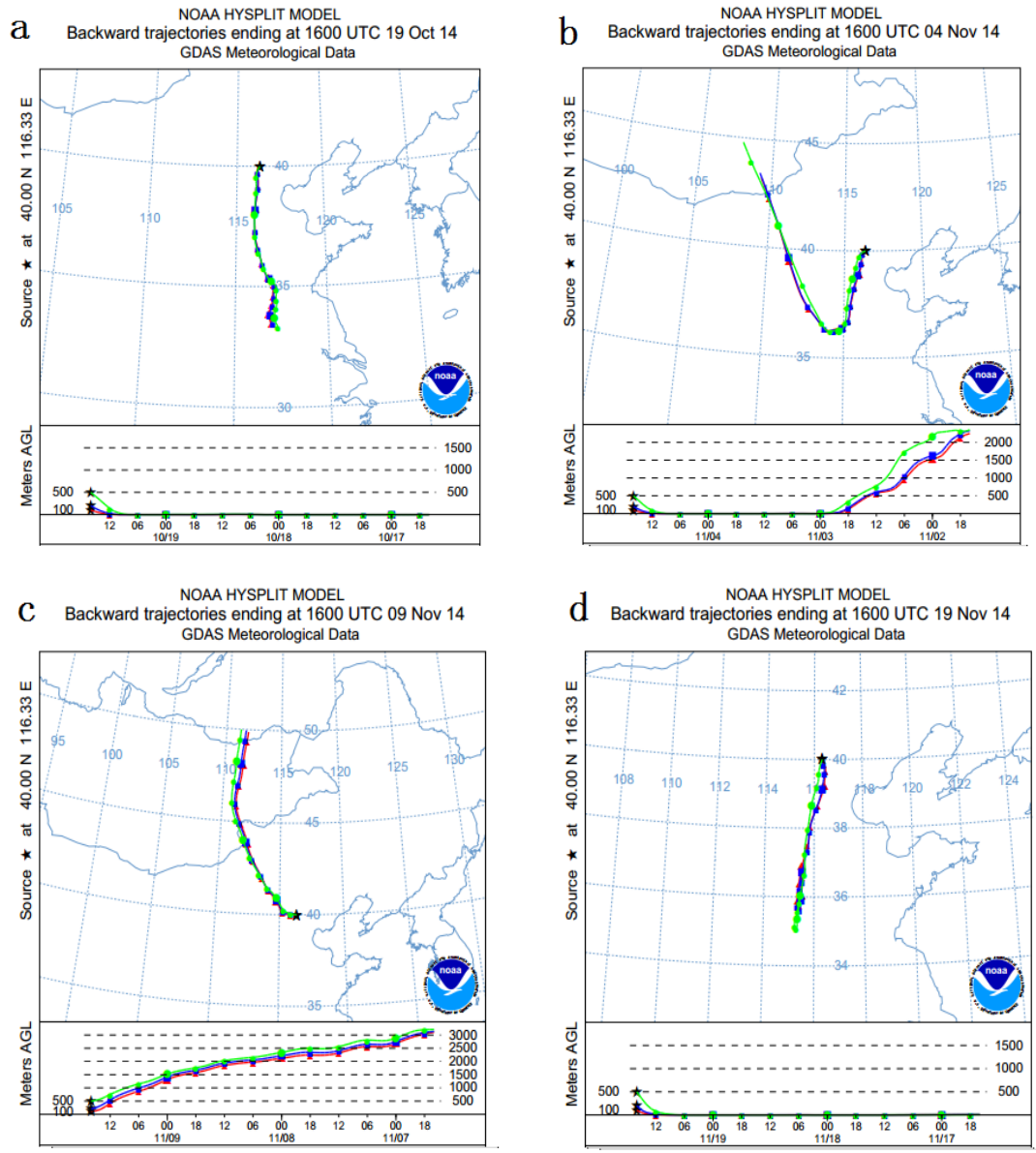
648 **Figure 2.** Mixing ratios of volatile organic compound (VOC) groups before,

649 during, and after the control period during APEC China 2014.



650

651 **Figure 3.** Time series of total measured volatile organic compounds (VOCs), temperature, wind direction, and speed at the PKU site during this  
 652 study.

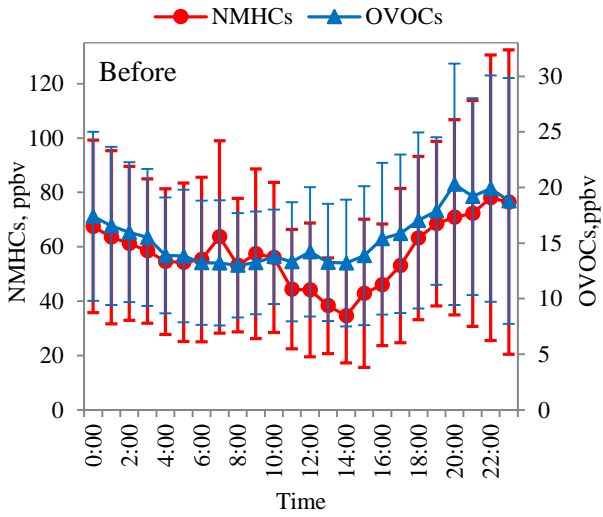


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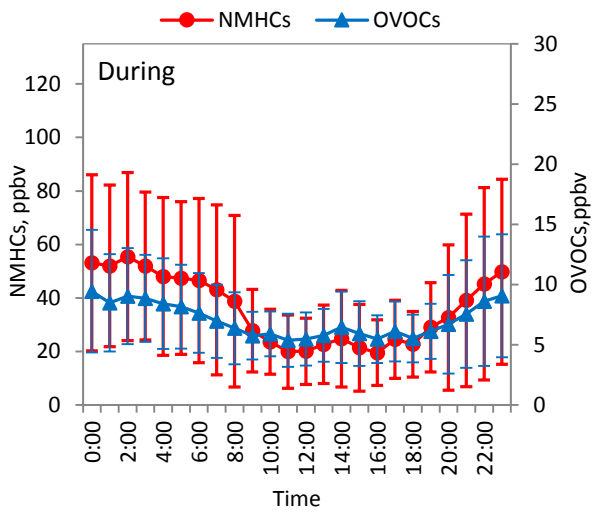
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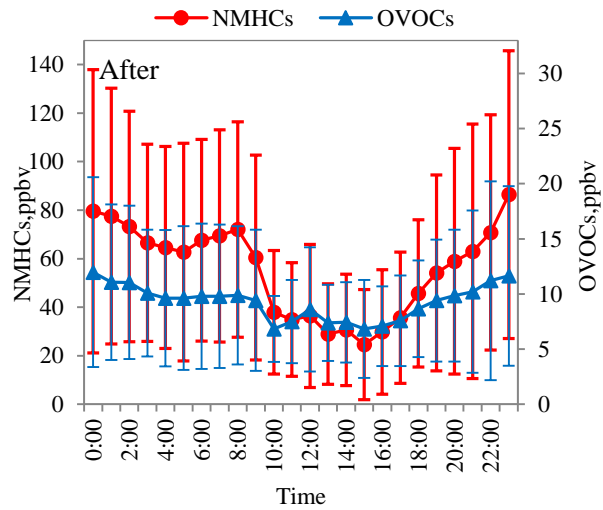
**Figure 4.** Three-day backward trajectories ending at 12:00 am (16:00 UTC) 19 October, and 4, 9, and 19 November 2014.



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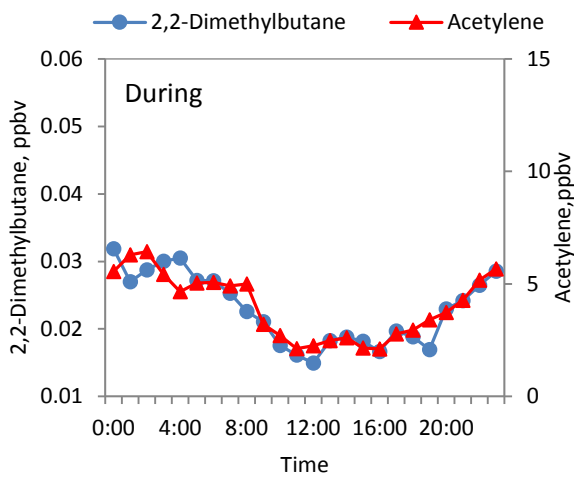
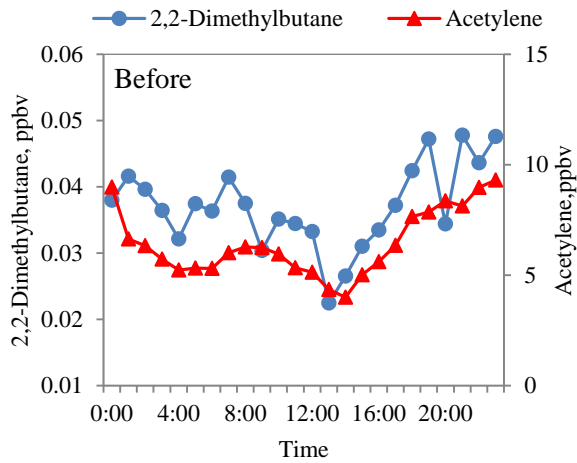
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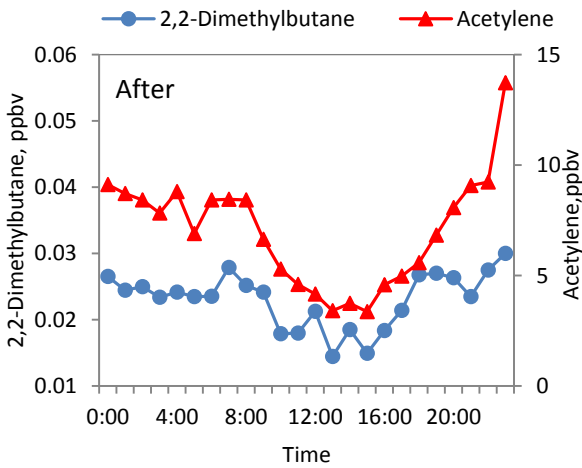
658

659 **Figure 5.** Diurnal variations in mixing ratios of  
 660 non-methane hydrocarbons (NMHCs) and  
 661 oxygenated volatile organic compounds (OVOC)  
 662 at the PKU site before, during, and after the control  
 663 period during APEC China 2014.





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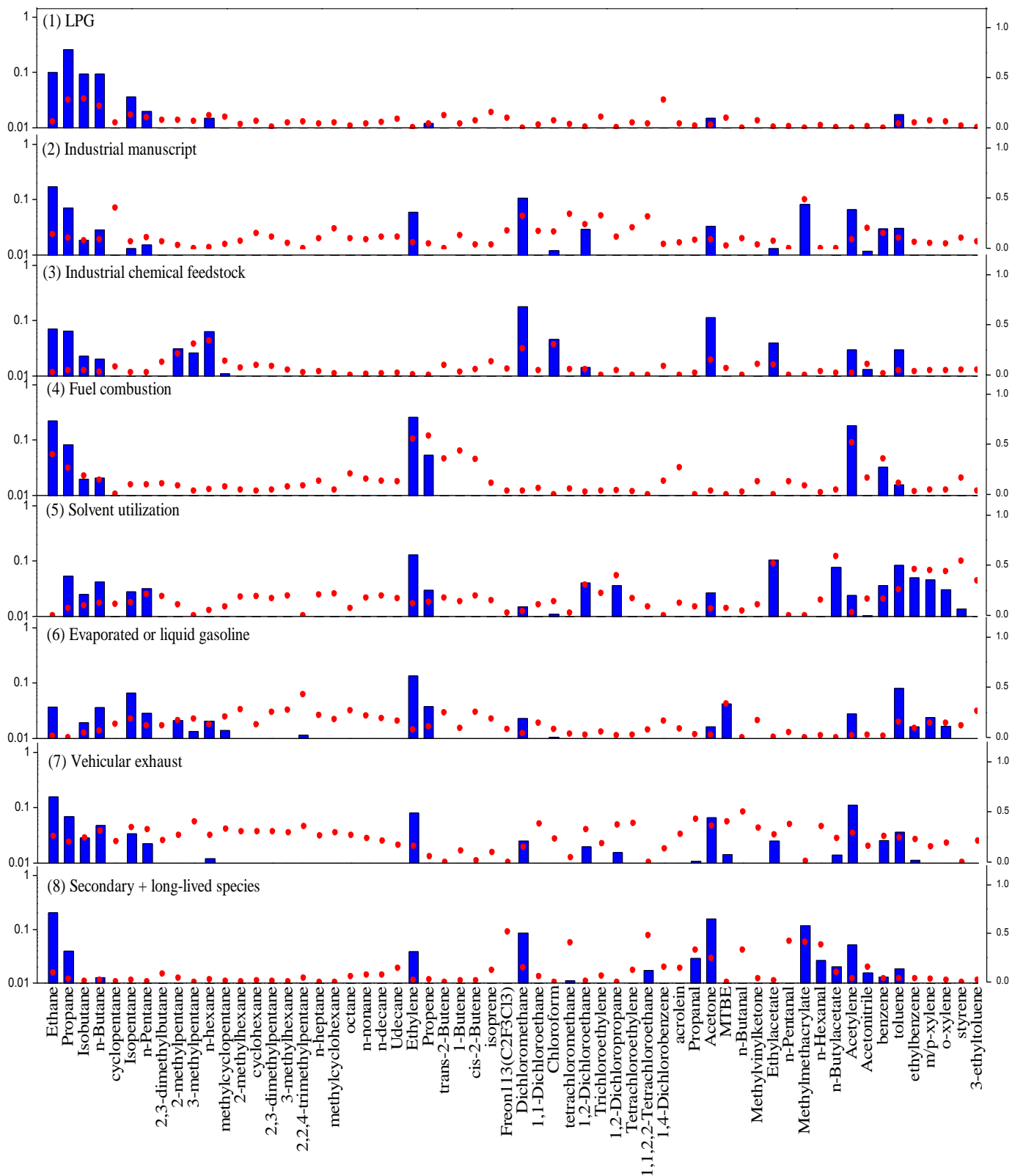
665

666 **Figure 6.** Diurnal variations of mixing ratios

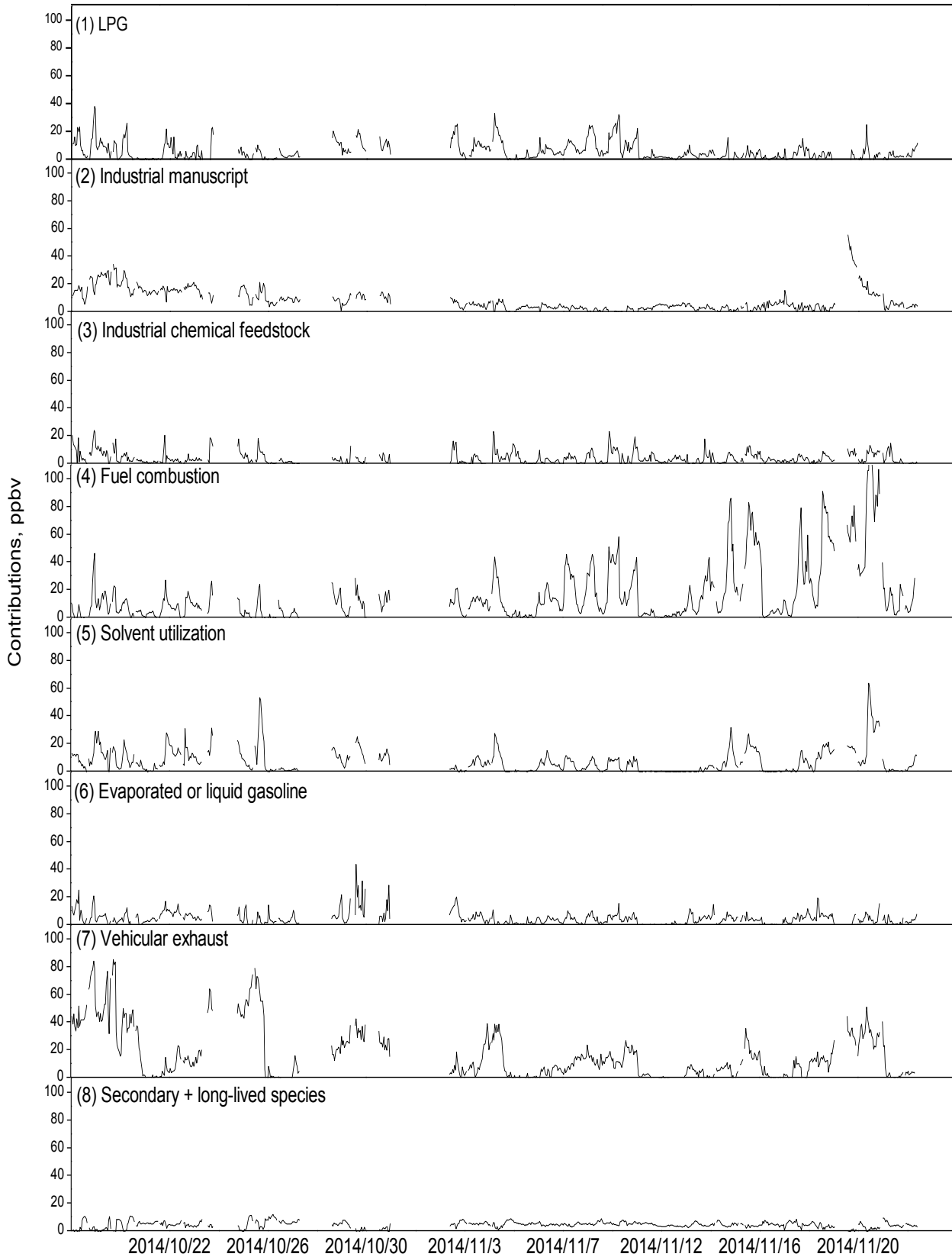
667 of 2,2-dimethylbutane and acetylene at the

668 PKU site before, during, and after the control

669 period during APEC China 2014.



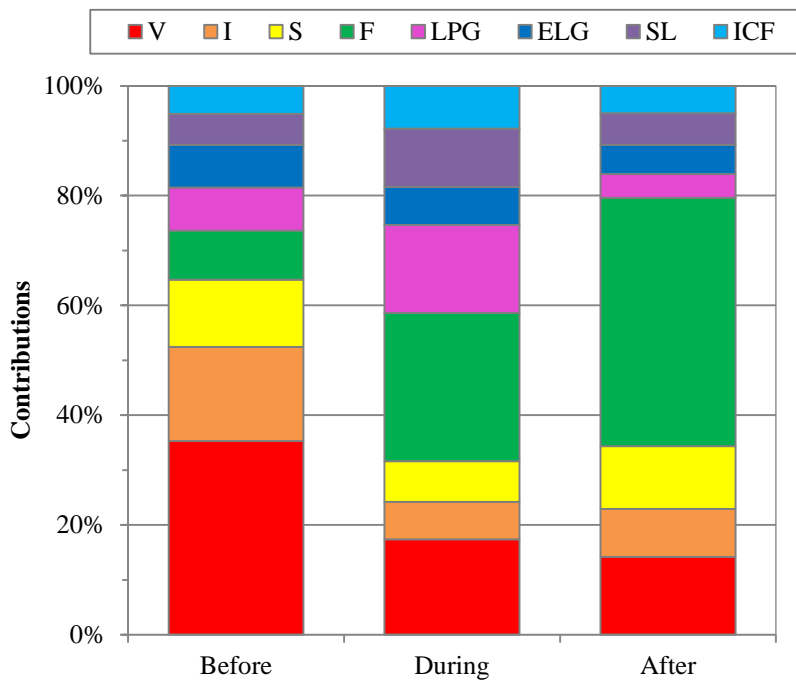
**Figure 7.** Eight source profiles (bars;  $\text{ppbv ppbv}^{-1}$ ) resolved from the PMF model, and contribution percentages (dots) from each source factor



673

674 **Figure 8.** Time series of hourly contributions from each identified source from 18 October to  
 675 22 November 2014.

676



677  
 678 **Figure 9.** Overall contributions (%) for the eight sources identified  
 679 by PMF analysis before, during, and after the control period during  
 680 the APEC China 2014. “V” stands for vehicular exhaust; “I” stands  
 681 for Industrial manufacturing; “S” stands for Solvent utilization; “F”  
 682 stands for fuel combustion; “LPG” stands for liquid petroleum gas;  
 683 “ELG” stands for Evaporated or liquid gasoline; “SL” stands for  
 684 secondary and long-lived species; “ICF” stands for industrial  
 685 chemical feedstock.