

# Sources of volatile organic compounds and policy implications for regional ozone pollution control in an urban location of Nanjing, East China

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**Abstract.** Understanding the composition, temporal variability, and source apportionment of volatile organic compounds (VOCs) is necessary for determining effective control measures to minimize VOCs and its related photochemical pollution. To provide a comprehensive analysis of VOC sources and their contributions to ozone (O<sub>3</sub>) formation in the Yangtze River Delta (YRD) - a region experiencing highest rates of industrial and economic development in China, we conducted a one-year sampling exercise using a thermal desorption-GC (gas chromatography) system for the first time at an urban site in Nanjing (JAES site). Alkanes were the dominant group at the JAES site, contributing ~53% to the observed total VOCs, followed by aromatics (~17%), acetylene (~17%), and alkenes (~13%). We identified seasonal variability in TVOCs with maximum and minimum concentrations in winter and summer, respectively. A morning and evening peak and a daytime trough were identified in the diurnal VOCs patterns. We identified VOC sources using positive matrix factorization and assessed their contributions to photochemical O<sub>3</sub> formation through calculating the O<sub>3</sub> formation potential (OFP) based on the mass concentrations and maximum incremental reactivities of VOCs. The PMF model identified five dominant VOC sources, with highest contributions from diesel vehicular exhausts (34 ± 5%), followed by gasoline vehicular exhausts (27 ± 3%), industrial emissions (19 ± 2%), fuel evaporation (15 ± 2%) and biogenic emissions (4 ± 1%). The results of the OFP calculation inferred that VOCs from industrial and vehicular emissions were found to be the dominance precursors for OFP, particularly the VOC species of xylenes, toluene and propene, which top priorities should be given to the alleviation of photochemical smog. Our results therefore highlight that priority should be given to limited VOC sources and species for effective control of O<sub>3</sub> formation in Nanjing.

## 1. Introduction

Volatile organic compounds (VOCs) are key precursors of O<sub>3</sub> and secondary organic aerosols (SOA) - a major component of fine particulate matter (PM<sub>2.5</sub>). VOCs significantly contribute to the formation of photochemical

36 smog, atmospheric oxidative capacity, visibility degradation, and global climate (Jenkin and Clemitshaw, 2000;  
37 Seinfeld and Pandis, 2006), and some VOCs are also known to be toxic to human health. Therefore, in recent  
38 years, much research has focused on the impacts of VOCs due to their influence on atmospheric chemistry and  
39 impacts on human health (Shao et al., 2009 and references therein).

40

41 The Yangtze River Delta (YRD) region (Shanghai-Jiangsu-Zhenjiang region) is one of the fastest growing  
42 regions in China, having recently undergone rapid urbanization and industrialization. Rapid economic growth  
43 has led to increased photochemical smog and elevated concentrations of ground-level O<sub>3</sub> and fine particulate  
44 matter (PM<sub>2.5</sub>). These conditions have been listed as the most important sources of pollution affecting the  
45 population in the YRD region, and are likely caused by increasing concentrations of VOCs. Therefore, it has  
46 been suggested that controlling VOC emissions is necessary for the effective alleviation of photochemical smog  
47 (Wang et al., 2009; Zhang et al., 2009; Cai et al., 2010; Kurokawa et al., 2013; Ding et al., 2016).

48

49 To further understand VOC characteristics and to develop effective policies towards lowering VOC emissions,  
50 a number of sampling campaigns have been conducted to investigate the components, mixing ratios,  
51 photochemical reactivity and emissions of VOCs over the YRD region (Cai et al., 2010; An et al., 2014; Mo et  
52 al., 2015; Pan et al., 2015; Shao et al., 2016; Xu et al., 2017). For example, based on continuous observation data  
53 collected from March, 2011 to February, 2012, An et al. (2014) identified clear seasonal VOC variability in an  
54 industrial area of Nanjing, with maximum and minimum levels observed in summer and winter, respectively.  
55 VOC variability was also found to be strongly influenced by industrial emissions. In contrast, Mo et al. (2017)  
56 found no difference in VOC chemical compositions between residential, industrial and suburban areas of the  
57 coastal industrial city, Ningbo. By comparing the emission-based profiles and those extracted from the positive  
58 matrix factorization (PMF) model, the petrochemical industry was identified as the highest contributor of  
59 ambient VOCs due to the unique industrial structure of Ningbo, which is a coastal city located on the southern  
60 wing of the Yangtze River Delta with petrochemical industry as its lead industry (Mo et al., 2015, 2016). Pan et  
61 al. (2015) conducted emissions measurements of open biomass burning in the rural area of the YRD region and  
62 examined the major contributors to O<sub>3</sub> pollution using a box model together with the Regional Atmospheric  
63 Chemical Mechanism. Overall, these studies were conducted in industrialized and/or rural areas of the YRD  
64 region and demonstrate the contribution of industrial emissions and biomass burning towards ambient VOC  
65 levels and their contributions to O<sub>3</sub> formation. However, VOC studies in urban areas of the YRD region are  
66 limited and could help to improve our understanding of the spatial variability of VOCs and their environmental  
67 impact, particularly as stricter policies on VOCs and/or photochemical smog have been implemented since 2013  
68 (Fu et al., 2016). Furthermore, the sampling resolution and sampling duration of these studies were relatively  
69 low as the samples were collected using canisters. High-resolution VOC datasets can provide more detailed  
70 information on the temporal and spatial variability, source apportionments, and impact factors of VOCs.

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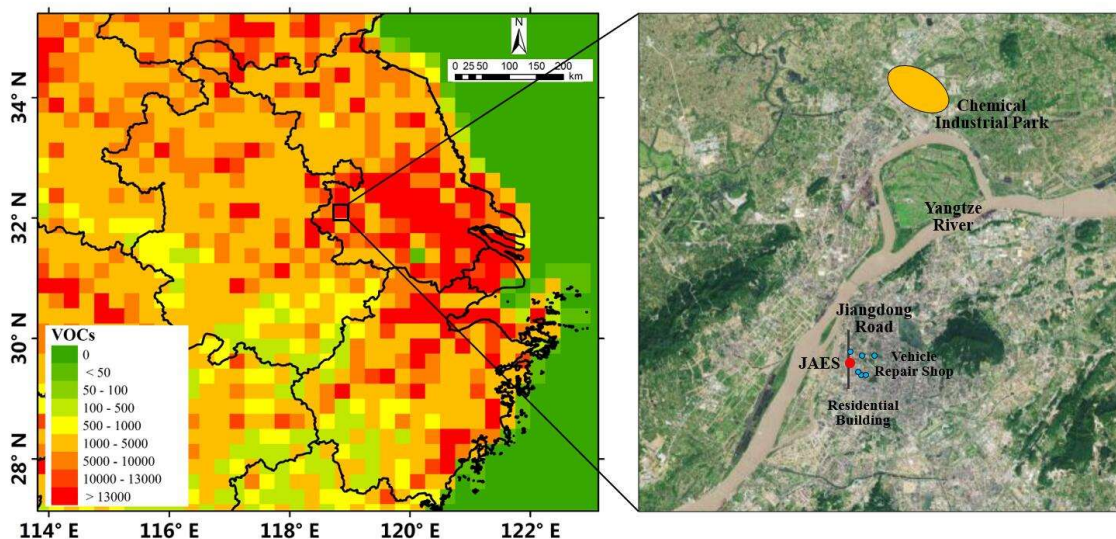
72 In this study, we collected continuous one-year observational VOC data at an urban site in Nanjing in the YRD  
73 region. The seasonal and diurnal characteristics of VOCs were investigated, and their sources were identified  
74 and quantified using the PMF model. Furthermore, we used a box model together with a Master Chemical  
75 Mechanism (MCM) (version 3.2) to identify the O<sub>3</sub>-precursor relationships and the contributions of VOC sources  
76 to photochemical O<sub>3</sub> formation. Our results were compared with VOCs data from other Chinese megacities.  
77 Based on these findings, we summarize and propose control strategies to minimize VOCs pollution and assess  
78 their implications for Nanjing and the wider YRD region. The results provide useful information towards  
79 lowering photochemical pollution in the YRD region as well as other regions in China.

## 80 **2. Methodology**

### 81 **2.1. Sampling campaign**

82 We continuously measured VOC concentrations from January to December, 2016, at an observation station on  
83 the rooftop of an office building (~80 m above the ground level) of the Jiangsu Academy of Environmental  
84 Science (JAES). There is a waterproof layer on the rooftop of the building but there was no guarantee that it was  
85 made of asphalt. Furthermore, despite this waterproof layer on the rooftop of the building, the interferences of  
86 emissions from this layer were believed to be insignificant because: 1) The waterproof layer was covered by the  
87 layer of concrete, which was further covered with a layer of ceramic tile; 2) The building had been built for three  
88 years before the sampling campaign was started; 3) It was documented that the VOC emitted from asphalt mainly  
89 included benzene, toluene, ethylbenzene and xylene (Gardiner and Lange, 2005). However, the levels of benzene,  
90 toluene, ethylbenzene, *m/p*-xylene and *o*-xylene were lower than those observed in other urban, industrial and  
91 rural environments in different regions (section 3.1, Zhang et al., 2012; An et al., 2014 and 2015; Mo et al., 2015,  
92 2017; He et al., 2019). 4) The sampling inlet was about 2-3 m above the rooftop of the building. It should be  
93 noted that there is a waterproof layer on the rooftop of the building. However, it is not sure that the waterproof  
94 layer was made of asphalt. Furthermore, though there is a waterproof layer on the rooftop of the building, the  
95 interferences of emissions from the layer were believed to be insignificant because: 1) The waterproof layer was  
96 covered by the layer of concrete, which was further covered with a layer of ceramic tile; 2) The building has  
97 been built for at least three years when the sampling campaign was started; 3) It was documented that the VOC  
98 emitted from asphalt mainly included benzene, toluene, ethylbenzene and xylene (Gardiner and Lange, 2005).  
99 However, the levels of benzene, toluene, ethylbenzene, *m/p*-xylene and *o*-xylene were lower than those observed  
100 in other urban and industrial and rural environments in different regions (Zhang et al., 2012; An et al., 2014 and  
101 2015; Mo et al., 2015, 2017; He et al., 2019) (details in section 3.1). 4) The sampling inlet were about 2-3 m  
102 above the rooftop of the building. The station is located in an urban area of Nanjing, and is surrounded by heavy  
103 road traffic, residential buildings, a plant and flower market, and several auto repair shops (Figure 1). Nanjing,  
104 located in the western part of the YRD region, is one of the most urbanized and industrialized areas in the world  
105 and consequently experiences severe air pollution. The site is located downwind of both Nanjing city center and

106 the wider YRD region (Zhao et al., 2017; Zhou et al., 2017), and is therefore ideally placed to determine the  
107 combined impacts of VOCs from both local and regional atmospheric pollution.



108  
109 **Figure 1. (a) Maps of the study location showing VOCs emission at a resolution of 0.25 degrees (MG/a) (The data were from**  
110 **MEIC emission inventory (www.meicmodel.org, last access date:15 September 2019). (b) The location of the JAES sampling**  
111 **site is indicated by a red circle (The base map was from © Baidu Maps). The blue circles indicate vehicle repair shops, the**  
112 **yellow circle indicates chemical industry park and the black solid line indicates a heavy traffic road**

113 Fifty-six VOC species including alkanes, alkenes, aromatics, and acetylene were measured at 1-h intervals using  
114 a PerkinElmer Online Ozone Precursor Analyzer based on a thermal desorption-GC (gas chromatography)  
115 system. First, the dried air samples were collected by a thermal desorption instrument and subsequently pre-  
116 concentrated onto a cold trap. The sampling flow was 15 mL/min. After 600 mL of air was sampled, the cold  
117 trap was heated to resolve the compounds adsorbed on to it. By applying the Dean's Switch technology whereby  
118 the technology that transfers the effluent from one column to another column with a different stationary phase,  
119 the low- and high-volatile components were injected into the  $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$  PLOT column ( $50\text{ m} \times 0.22\text{ mm} \times$   
120  $1\text{ }\mu\text{m}$ ) and the dimethyl siloxane column ( $50\text{ m} \times 0.32\text{ mm} \times 1\text{ }\mu\text{m}$ ), respectively, and analyzed using a flame  
121 ionization detector (FID). The temperature increased from 46 °C for 15 min to 170 °C at a rate of 5 °C/min, and  
122 then to 200 °C at a rate of 15 °C/min. The samples were finally held at 200 °C for 6 min.

123  
124 A calibration was performed daily for quality control. The calibration curves showed good linearity with a  
125 correlation coefficient of 0.99. Seven analyses were performed repeatedly to test the precision of the 56 species.  
126 Calibrant concentrations in the gas standard mixture (56  $\text{C}_2\text{-C}_{12}$  NMHCs, Linde Spectra Environment Gases, Inc,  
127 USA) ranged from 20 to 49 ppbC. The relative standard deviations of most of the 56 species were <5%,  
128 representing an error of <0.5 ppb.

129 On the other hand, trace gases including CO, NO-NO<sub>2</sub>-NO<sub>x</sub>, SO<sub>2</sub>, and O<sub>3</sub> were measured at 1-min resolution  
130 using the commercial instruments of TEI 48i, 42i, 43i and 49i (Thermo Electron Corporation). All these  
131 instruments were zero checked daily, span calibrated weekly and multi-point calibrated monthly. Furthermore,

132 meteorological conditions, including the temperature, relative humidity, pressure, wind speed and direction were  
133 monitored at 1-min resolution by a weather station (Vantage Pro TM & Vantage Pro 2 plus TM Weather Stations,  
134 Davis Instruments).

## 135 **2.2. The PMF model for VOC source identification**

136 In this study, the US EPA PMF (version 4.1) model, which has been widely used to conduct source apportionment  
137 of VOCs (Zhang et al., 2013; Mo et al., 2017; He et al., 2019 and references therein), was applied to the observed  
138 VOC data to identify potential VOC sources. A detailed description of the PMF model is provided by Yuan et al.  
139 (2009) and Ling et al. (2011). In brief, the PMF model is a receptor model, which can identify the sources and  
140 contributions of given species without prior input of their source profiles. In this study, a total of 25 species were  
141 selected as the input for the PMF model including species with high abundances as well as typical tracers of  
142 emission sources. Species with high percentages of missing values (> 25%) were excluded (i.e., 1,3-butadiene,  
143 cis/trans-2-pentene, dimethylpentane, and trimethylpentane). The total concentration of the 25 selected species  
144 accounted for ~92% of the total measured VOC composition. Furthermore, we calculated the total reactivity of  
145 the selected 25 species to be ~90% of the total measured VOCs through the analysis of maximum incremental  
146 reactivity (MIR) (Shao et al., 2009a). The high abundance and total reactivity contributions suggests that the  
147 selected 25 species were appropriate for the PMF model simulation.

148  
149 The PMF model was tested using a variety of factor numbers, and the optimum source profiles and contributions  
150 were determined based on the correlation between modelled and observed data, the comparison of modelled  
151 profiles with the results from emission-based measurements, and previous studies involving PMF/other receptor  
152 model simulations (i.e., HKEPD, 2015; Wang et al., 2014; An et al., 2014; Liu et al., 2008a). For example,  
153 different solution with different factor numbers was explored and the source apportionment results from a five-  
154 factor resolution that could sufficiently explain the observed levels of VOCs were selected (details in Section  
155 3.3). Compared with five-factor solution, the four-factor solution derived two profiles that attributable to gasoline  
156 and diesel vehicular exhaust, while most of the aromatic species in these sources and certain amounts of C<sub>3</sub>-C<sub>4</sub>  
157 species from fuel evaporation were categorized under industrial emission. On the other hand, the six-factor  
158 solution has split a factor with high presence of ethyne and certain amounts of ethane (30% in species total), C<sub>3</sub>  
159 species and benzene (~20% in species total), while some alkenes (18-80% in species total) were incorporated  
160 into fuel evaporation. Furthermore, the performance of the five-factor solution was evaluated using various  
161 checks and sensitivity tests. Suitable correlations between the observed concentrations and those of each species  
162 predicted by the model were observed, with the correlation coefficients (R<sup>2</sup>) ranging from 0.60 - 0.91, indicating  
163 that the solution adequately reproduced the observed variations of each species. All the scale residuals were  
164 within ± 3σ with normal distributions for all species (Baudic et al., 2016). Moreover, different numbers of start  
165 seeds were tested during the simulation and no-multiple solutions were found. The ratio of Q(robust)/Q(true)  
166 obtained was ~0.93, close to 1 as suggested by previous studies and the user guide manual (Paatero, 2000; Lau

167 et al., 2010; Ling et al., 2016). In addition, the results from bootstrapping analysis for the five-factor solution  
 168 with bootstrap random seed found that all the factors were mapped to a basic factor in all the 20 bootstrap runs,  
 169 while the uncertainties of each species from bootstrapping analysis were within the range of 1~20%. In this study,  
 170 different  $F_{\text{peak}}$  values ranging from -5 to 5 was tested in the 5-factor solution for a more realistic profile (Lau et  
 171 al., 2010; Baudic et al., 2016). The profiles with the nonzero  $F_{\text{peak}}$  values were consistent with those with zero  
 172  $F_{\text{peak}}$  value, reflecting that there was little rotation for the selected solution, confirming that the profiles were  
 173 reasonably explained by the five-factor solution (Baudic et al., 2016). The results of  $F_{\text{peak}}$  value = 0.5 (the base  
 174 run) was selected for analysis in this study. Overall, the above features demonstrated that the five-factor solution  
 175 from PMF could provide reasonable and stable apportionment results for the observed VOCs at the JAES site.

### 176 3. Results and discussion

#### 177 3.1 VOC observation statistics

178 Table 1 shows the average concentration and standard deviation of fifty-six VOC species concentrations  
 179 measured at the JAES site, while Figure S1 in the supplementary presented the time series of all pollution data  
 180 collected at the JAES site. The annual average total VOC (TVOC, sum of the measured VOCs) concentrations  
 181 in 2016 was  $25.7 \pm 19.1$  ppbv, with highest contributions from alkanes ( $13.6 \pm 10.5$  ppbv, ~53%), followed by  
 182 aromatics ( $4.4 \pm 4.0$  ppbv, ~17%), acetylene ( $4.5 \pm 5.5$  ppbv, ~17%) and alkenes ( $3.2 \pm 3.3$  ppbv, ~13%).  
 183 Annually, the most abundant 10 species were acetylene, propane, ethane, ethylene, butane, toluene, *i*-pentane, *i*-  
 184 butane, propylene and benzene, with a combined contribution of ~77% of the TVOC. This observed VOC  
 185 composition suggests that VOCs at the JAES site are predominantly sourced from combustion emissions (i.e.,  
 186 vehicular emissions). Alkenes are mainly associated with vehicular emissions and are more photochemically  
 187 reactive relative to alkanes and aromatics. The alkenes were found to have higher mixing ratios during weekdays  
 188 relative to the weekends ( $3.5 \pm 0.2$  vs  $2.9 \pm 0.1$  ppbv for weekdays and weekend, respectively,  $p < 0.05$ ), further  
 189 confirming the dominant contribution of vehicular emissions to VOC levels at the JAES site.

190  
 191 **Table 1. The average mixing ratios and standard deviation of VOC species concentrations measured at the JAES site from**  
 192 **January to December 2016.**

Species	Average $\pm$ Standard deviation (ppbv)	Species	Average $\pm$ Standard deviation (ppbv)
<b>Alkanes</b>	<b><math>13.64 \pm 10.53</math></b>	<b>Alkenes</b>	<b><math>3.24 \pm 3.28</math></b>
ethane	$3.63 \pm 2.68$	ethene	$1.72 \pm 2.00$
propane	$3.70 \pm 3.01$	propylene	$0.92 \pm 1.16$
<i>i</i> -butane	$1.03 \pm 0.87$	1-butene	$0.12 \pm 0.16$
<i>n</i> -butane	$1.55 \pm 1.26$	<i>cis</i> -2-butene	$0.06 \pm 0.09$
cyclopentane	$0.08 \pm 0.10$	<i>trans</i> -2-butene	$0.16 \pm 0.11$
<i>i</i> -pentane	$1.15 \pm 1.24$	1-pentene	$0.03 \pm 0.03$
<i>n</i> -pentane	$0.61 \pm 0.60$	<i>cis</i> -1-pentene	$0.02 \pm 0.03$

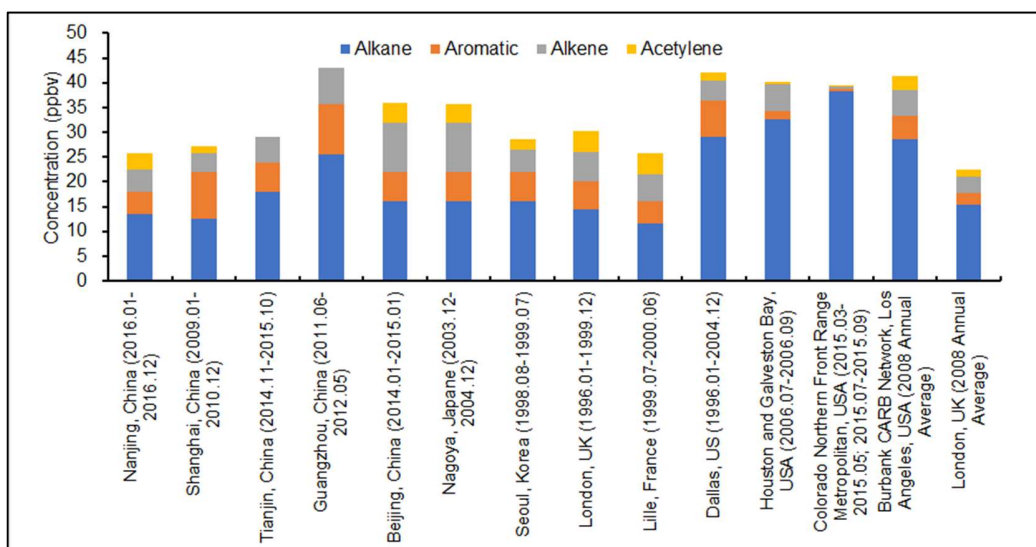
2,2-dimethylbutane	0.02 ± 0.02	<i>trans</i> -2-pentene	0.02 ± 0.03
2,3-dimethylbutane	0.05 ± 0.07	isoprene	0.14 ± 0.20
2-methylpentane	0.26 ± 0.29	<i>n</i> -hexene	0.05 ± 0.03
3-methylpentane	0.16 ± 0.21	<b>Aromatics</b>	<b>4.40 ± 4.01</b>
<i>n</i> -hexane	0.40 ± 0.45	benzene	0.80 ± 0.70
methylcyclopentane	0.26 ± 0.27	toluene	1.40 ± 1.35
cyclohexane	0.10 ± 0.16	ethylbenzene	0.50 ± 0.62
2,4-dimethylpentane	0.03 ± 0.01	<i>m/p</i> -xylene	0.70 ± 0.71
2,3-dimethylpentane	0.03 ± 0.02	<i>o</i> -xylene	0.25 ± 0.24
2-methylhexane	0.06 ± 0.09	styrene	0.12 ± 0.17
3-methylhexane	0.07 ± 0.10	<i>n</i> -propylbenzene	0.03 ± 0.03
heptane	0.09 ± 0.11	<i>i</i> -propylbenzene	0.03 ± 0.04
methylcyclohexane	0.07 ± 0.09	<i>m</i> -ethyltoluene	0.11 ± 0.14
2,2,4-trimethylpentane	0.02 ± 0.03	<i>p</i> -ethyltoluene	0.05 ± 0.07
2,3,4-trimethylpentane	0.02 ± 0.01	<i>o</i> -ethyltoluene	0.04 ± 0.05
2-methylheptane	0.02 ± 0.02	1,3,5-trimethylbenzene	0.04 ± 0.06
3-methylheptane	0.02 ± 0.02	1,2,4-trimethylbenzene	0.15 ± 0.21
octane	0.04 ± 0.06	1,2,3-trimethylpentane	0.10 ± 0.14
nonane	0.02 ± 0.02	<i>m</i> -diethylbenzene	0.03 ± 0.06
decane	0.04 ± 0.04	<i>p</i> -diethylbenzene	0.04 ± 0.08
undecane	0.04 ± 0.07	<b>Acetylene</b>	<b>4.47 ± 5.49</b>
dodecane	0.09 ± 0.20	--	--

193  
194 The TVOC level in this study was lower than previous measurements from an industrial site in Nanjing, in which  
195 43.5 ppbv TVOC was reported (An et al., 2014). However, the high TVOC levels are likely due to the proximity  
196 of the observation site (~3 km northeast) to the Nanjing chemical industry area, as well as several iron, steel, and  
197 cogeneration power plants (within 2 km) (An et al., 2014). The variability in land-use between these two studies  
198 have also resulted in distinct VOC component profiles. In the industrial area, the relative contributions of alkenes  
199 and aromatics were as high as 25% and 22%, while the contribution of alkynes was only 7% (An et al., 2014).  
200 The alkane, alkene, and aromatic concentrations from the industrial site were 1.4, 3.4, and 2.2 times higher than  
201 the concentrations of this study, respectively, while alkyne concentrations were ~30% lower. Given the large  
202 variability observed between the two sites, it is crucial to assess the spatial variability of ambient VOCs across  
203 the city through a collaboration of multiple research groups using available real-time and online VOC monitoring  
204 systems.

205  
206 Table S1 compares reported ambient VOCs from continuous measurements of ≥1 year in several megacities in  
207 a number of countries, including China. Continuous online measurements of ambient VOCs have only been  
208 available in China since 2010, unlike many developed countries whereby online VOC measurements have been  
209 available for multiple decades. In China, such measurements are only concentrated in a few megacities, including  
210 Beijing, Guangzhou, and Shanghai. The TVOC level reported in Nanjing was close to levels measured in

211 Shanghai (another megacity in the YRD, East China, 27.8 ppbv) (Wang et al., 2013), Tianjin (a megacity in  
212 North China, 28.7 ppbv) (Liu et al., 2016), and Wuhan (a megacity located in central China, 24.3 ppbv) (Lyu et  
213 al., 2016), but was considerably lower than Beijing (north China, 35.2 ppbv) (Zhang et al., 2017) and Guangzhou  
214 (south China, 42.7 ppbv) (Zou et al., 2015). Alkanes were the dominant hydrocarbon group in all the cities;  
215 however, some differences in relative contributions of the four classes were observed. The contribution from  
216 aromatics was highest in Shanghai (31%) relative to the other cities, which is likely explained by the large  
217 petrochemical and steel industry in Shanghai (Huang et al., 2011; Wang et al., 2013). In comparison, the  
218 contribution of aromatics in Guangzhou (Zou et al., 2015) and the industrial area in Nanjing (An et al., 2014)  
219 were 24% and 22%, respectively, while in other cities the contribution ranged between 17-19%. The current  
220 ambient VOC concentrations in Chinese megacities are generally comparable to the urban VOC levels in  
221 developed countries during the year 2000. However, in developed countries, the mixing ratios of VOCs were  
222 observed to decrease in the recent decades following the implementation and formulation of VOC strategies  
223 (Warneke et al., 2012). For example, the mixing ratios of VOCs in Los Angeles have decreased significantly  
224 from 1960-2002 at an average annual rate of ~7.5%, while the mixing ratios of VOCs in London presented a  
225 higher and faster decreased since 1998 when there were higher VOC mixing ratios than those in Los Angeles,  
226 confirming that the earlier implementation of VOC reduction strategies in California had clearly led to the earlier  
227 improvement of air quality compared to London (Warneke et al., 2012; von Schneidemesser et al., 2010).  
228 Chinese megacities are therefore experiencing significantly higher ambient VOCs contamination, given the  
229 remarkable decrease in VOC emissions in developed countries over the last two decades (Pan et al., 2015;  
230 European Environment Agency, 2016; U.S. EPA, 2017;). High VOC levels in Chinese megacities are known to  
231 impact ambient ozone and secondary particle pollution, as well as cause adverse impacts on human health.  
232 However, as China has a solid foundation for VOCs monitoring and control, numerous strict, appropriate and  
233 targeted reduction strategies for VOCs have been/are being formulated and implemented in Chinese megacities  
234 (Guo et al., 2017). It is expected these measures could help China to reduce VOC emissions/mixing ratios and  
235 improve air quality in the future.





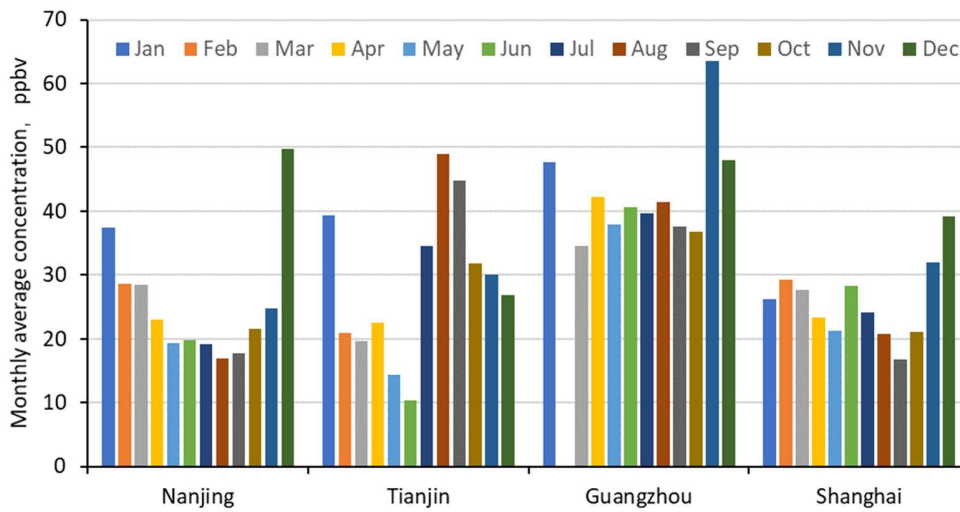
236  
237 **Figure 2. Comparison of annual average concentrations of ambient VOC in different cities based on real-time online**  
238 **continuous measurements of at least one year.**

239 **3.2 Temporal variability**

240 In this study, ambient VOCs showed significant seasonal variability, with relatively high monthly average  
241 concentrations in winter ( $40.2 \pm 24.0$  ppbv) and spring ( $23.8 \pm 15.0$  ppbv), and low concentrations in summer  
242 ( $18.5 \pm 14.6$  ppbv) and autumn ( $20.1 \pm 12.2$  ppbv). As shown in Figure S2, the highest monthly average  
243 concentration was observed in December, followed by January. High pollution levels during the winter period  
244 are usually expected and is explained by atmospheric temperature inversions caused by cooler weather, which  
245 inhibits particle dispersion. Lower concentrations during the summer period are due to both favorable diffusion  
246 conditions and photochemical degradation of VOCs.

247  
248 High wintertime VOCs pollution were also reported in Shanghai (Wang et al., 2013), Guangzhou (Zou et al.,  
249 2015), and Tianjin (Liu et al., 2016), though some differences in the monthly VOC variability were also observed.  
250 Except for the winter months, similar (and relatively stable) ambient VOC levels in the remaining months were  
251 observed for Guangdong (Figure 3). In Shanghai, relative high levels of VOCs were observed from October to  
252 January of the following year and from June to July based on the two-year measurement conducted from 2009  
253 to 2010 (Wang et al., 2013). The inversion layer, the effect of cold front or uniform pressure in winter resulted  
254 in high levels of VOCs from October to January of the following year, while the frontal inverted trough or  
255 frequently observed stagnant high pressure system with southwest flow that could lead to poor diffusion were  
256 unfavorable meteorological conditions for high VOC levels from June to July. In addition, air masses transported  
257 from upwind chemical and petrochemical industrial factories located in the southwest and south of the  
258 monitoring site was another factor for the high VOC levels in summer (*i.e.*, June and July) and winter. VOCs  
259 concentrations in Tianjin showed significant monthly variability. Highest concentrations were reported in  
260 autumn and lowest concentrations were reported in summer. The observed monthly variability is affected by

261 several factors including the type and level of emissions and local meteorological conditions.



262  
263 **Figure 3. Monthly variability of ambient VOCs at the JAES site and three other Chinese cities, Shanghai (Wang et al., 2013),**  
264 **Guangzhou (Zou et al., 2015), and Tianjin (Liu et al., 2016).**

265 Figure S3 shows the diurnal trends in ambient VOCs for each month. The diurnal patterns were generally similar  
266 for all the months. The observed peak at approximately 8-9 am (local time) corresponds with the city's morning  
267 traffic rush. The concentration begins to decrease after 9 am, with lowest concentrations observed at  
268 approximately 3 pm. The observed decline was likely due to reduced vehicle emissions, growth of the inversion  
269 top, and enhanced photochemical VOC degradation. After 3 pm, the concentrations begin to increase gradually  
270 as a result of increased vehicle emissions during the evening rush hour, as well as a reduction in the atmospheric  
271 mixing height under evening meteorological conditions. The second evening VOC peak was less prominent than  
272 the morning peak. Evening concentrations were generally higher than the daytime concentrations, and the  
273 amplitudes of diurnal variability were larger in autumn and summer compared to winter and spring.

274

### 275 3.3 Source apportionment of VOCs

276 In this study, we applied the PMF model to apportion the sources of VOCs at the sampling site. Figure 4  
277 illustrates the source profiles of the VOCs produced by the PMF model. Five VOC sources were resolved by  
278 PMF, including biogenic emissions (Source 1), fuel evaporation (Source 2), gasoline vehicular exhausts (Source  
279 3), diesel vehicular exhausts (Source 4), and industrial emissions (Source 5).

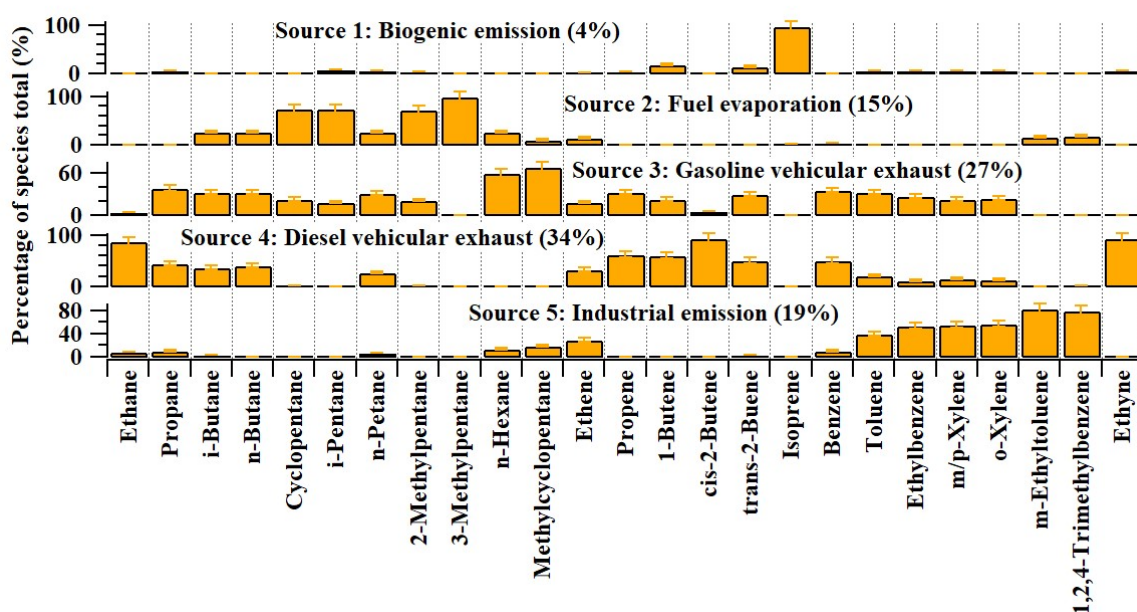
280

281 Source 1 was identified as biogenic emissions due to the high loading of isoprene – a typical tracer of biogenic  
282 emissions (Lau et al., 2010; Yuan et al., 2012). Source 2 was represented by high proportions of 2-methylpentane,  
283 3-methylpentane, *i*-pentane, and cyclopentane. Pentanes are mainly associated with profiles from gasoline-  
284 related emissions (Barletta et al., 2005; Tsai et al., 2006). However, the low contributions of incomplete  
285 combustion tracers in this profile suggested that the VOCs were sourced from fuel evaporation. The high

286 presence of pentanes in this profile was consistent with the source profile of gasoline volatilization extracted  
287 from principal component analysis/absolute principal component scores (PCA/APCs) based on the observed  
288 VOC data collected in an industrial area of Nanjing (An et al., 2014), the source profile of gasoline evaporation  
289 from PMF at the suburban site and urban site in Beijing and Hong Kong (Yuan et al., 2009; Lau et al., 2010).  
290 Particularly, based on the emission-based measurement, Liu et al. (2008b) conducted source apportionments of  
291 VOCs in the Pearl River Delta region by the chemical mass balance (CMB) receptor model, which attributed the  
292 source with high loadings of *n/i*-pentanes, cyclopentane and 2/3-methylpentane as gasoline evaporation.  
293 Therefore, Source 2 here was identified as fuel evaporation.

294  
295 Source 3 and Source 4 were identified as vehicular exhausts due to their high loadings of incomplete combustion  
296 tracers, i.e., C<sub>2</sub>-C<sub>4</sub> alkanes and alkenes (Guo et al., 2011a, b; Zhang et al., 2018). Zhang et al. (2018) compared  
297 the VOC composition of vehicular emissions from Zhujiang Tunnel in 2014 and 2004 in the Pearl River Delta  
298 region with those from other tunnel measurements. C<sub>2</sub>-C<sub>4</sub> alkanes and alkenes were found to made the greatest  
299 contributions to the loading of VOCs emitted from vehicles in 2014. The higher proportions of *n/i*-pentane, *n*-  
300 hexane, and methylcyclopentane in Source 3 relative to Source 4 indicated VOCs sourced from gasoline  
301 vehicular exhausts (Liu et al., 2008b; Guo et al., 2011b; Zhang et al., 2018). Source 4 was identified as diesel  
302 vehicular exhausts due to the high percentages of ethyne, ethane, and propene, as well as C<sub>2</sub>-C<sub>4</sub> alkenes (Ho et  
303 al., 2009; Cai et al., 2010; Ou et al., 2015; Liu et al., 2008c). Source 5 was characterized by high concentrations  
304 of aromatics. In addition to gasoline vehicle emissions, industrial emission could be another important  
305 contributor to ambient aromatic hydrocarbons in the Yangtze River Delta, Pearl River Delta and North China  
306 Plain (Yuan et al., 2009; Zhang et al., 2013, 2014; An et al., 2014; Mo et al., 2015, 2017; He et al., 2019). The  
307 tunnel studies and emission-based measurement results found that aromatic hydrocarbons from gasoline vehicle  
308 exhaust were coherently emitted with pentanes, butenes, *n*-hexane, and cyclopentane, which were more  
309 consistent with the profile in source 3 mentioned above (Liu et al., 2008; Ho et al., 2009; Yuan et al., 2009;  
310 Zhang et al., 2018). Therefore, the absence of above species in source 5 indicated that this source could be related  
311 to industrial emission (Zhang et al., 2014). Particularly, the high presence of toluene, ethylbenzene, xylenes,  
312 ethyltoluene and trimethylbenzene was consistent with the emission-base measurement results conducted in  
313 paint and printing industries (Yuan et al., 2010) and manufacturing facilities (Zheng et al., 2013). On the other  
314 hand, the profile of high presence of aromatic hydrocarbons (C<sub>7</sub>-C<sub>9</sub> aromatics) and the certain amount of ethene,  
315 was also agree with the profiles measured in the areas dominated by industrial emissions in the Yangtze River  
316 Delta region (An et al., 2014; Shao et al., 2016; Mo et al., 2017). For example, An et al. (2014) reported that  
317 toluene, ethylbenzene, xylenes, and trimethylbenzenes could be emitted from different industrial processes, and  
318 identified that the factors with high loadings of these species as industrial production, solvent usage and  
319 industrial production volatilization sources by PAC/APCS at the industrial area in Nanjing. On the other hand,  
320 Mo et al. (2017) identified the factors with high concentrations of C<sub>7</sub>-C<sub>9</sub> aromatics and ethene as residential  
321 solvent usage, chemical and paint industries and petrochemical industry with the PMF model applied to the data

322 collected in an industrialized coastal city of Yangtze River Delta region. To further identify source 3 and source  
 323 5, the ratio of toluene/benzene (T/B, ppbv/ppbv) in each profile was compared with those obtained from  
 324 emission-based measurements and tunnel study results (Zhang et al., 2018 and references therein). The ratios of  
 325 T/B were ~8.2 and ~1.2 for sources 5 and 3, respectively, and were consistent with those of “industrial processes  
 326 and solvent application”, and “roadside and tunnel study”, respectively (Zhang et al., 2018 and references  
 327 therein). This further confirmed that source 3 was related to gasoline vehicular exhaust, while source 5 was  
 328 associated with industrial emission.



329  
 330 **Figure 4. Source profiles of VOCs identified using the PMF model and the relative contributions of the individual VOC**  
 331 **species.**

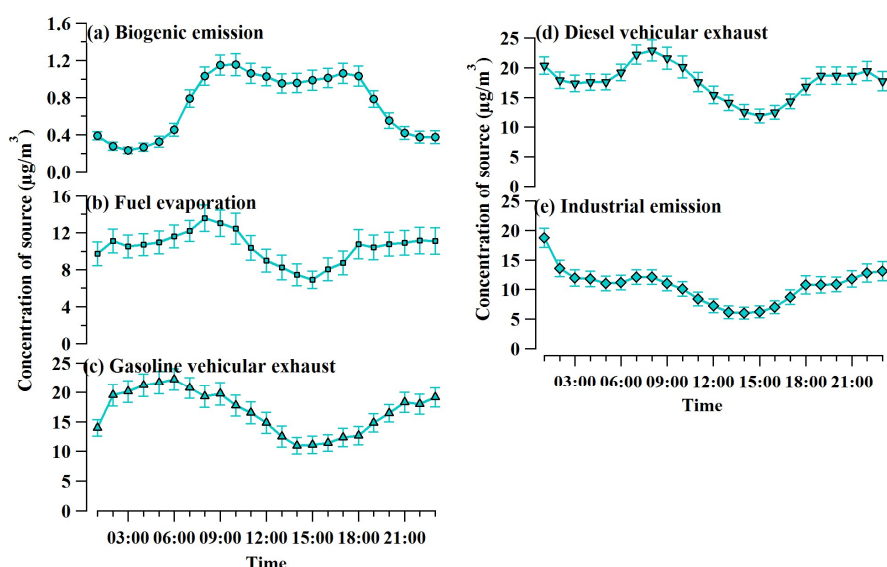
332  
 333 Vehicular exhausts were found to be the most significant contributor to the TVOCs at the JAES site, with average  
 334 contributions of ~34% and ~27% for diesel and gasoline exhausts, respectively, followed by industrial emissions  
 335 (19%), fuel evaporation (~15%), and biogenic emissions (~4%). Our results are inconsistent with previous results  
 336 observed at industrial sites in Nanjing (An et al., 2014; Xia et al., 2014a). An et al. (2014) found that industrial  
 337 activities were the most significant source of VOCs, contributing 45%-63% (mainly aromatic VOCs), followed  
 338 by vehicle emission at 34%-50%. Similarly, Xia et al. (2014a) reported solvent usage and other industrial sources  
 339 to account for most (31%) of the VOCs in a suburban site in southwestern Nanjing, close in proximity to  
 340 Nanjing’s industrial zone. Fossil fuel/biomass/biofuel combustion were the second highest contributors at 28%,  
 341 while the average contribution of vehicular emissions was 17%, mainly from the northern center of Nanjing (Xia  
 342 et al., 2014a). Combined, these results infer vehicular emissions to be a major component of urban emissions in  
 343 Nanjing. The observed spatial variability in the contributions of VOC sources infers the complex emissions  
 344 characteristics of VOCs in Nanjing, likely due to the city’s unique industrial structure. For example, the sampling  
 345 site (i.e., the JAES site) was located at a more residential and urban area compared to other sites listed in An et

346 al. (2014) and Xia et al. (2014). There are more than 0.22 million people living in the areas surrounding the  
347 sampled site (within 3 km of the observation site) which composed of residential communities, schools,  
348 government agencies, and business centers. These results also demonstrate that local emissions are dominant  
349 contributors to ambient VOCs levels in Nanjing.

350  
351 The dominant contribution of vehicular emissions to ambient VOCs in Nanjing is consistent with the  
352 urban/central areas of other large cities, including Hong Kong, Guangzhou, Shanghai, and Beijing, as identified  
353 and quantified by the PMF model (Yuan et al., 2009; Cai et al., 2010; Guo et al., 2011a; Zhang et al., 2013; Wang  
354 et al., 2015). In addition, our results are in agreement with the anthropogenic VOC source emission inventory of  
355 Jiangsu Province in 2010 (Xia et al., 2014b), indicating vehicular emissions and industrial emissions (i.e., solvent  
356 usage and industrial process source) to be the two dominant sources of VOCs in the region. However, the  
357 contributions of vehicle related emissions (i.e., ~25%) and industrial emissions were lower and higher than those  
358 quantified by the PMF model in this study, respectively. The observed discrepancy between the two studies may  
359 be due to differences in source categories, measured VOC species, and/or sampling locations and methods used  
360 in the different models. For example, the VOC sources in Jiangsu province were categorized into vehicular  
361 related emission (~26%), industrial solvent usage (~25%), fossil fuel combustion (~24%), industrial processes  
362 (~22%) and biomass burning (~3%). Further, vehicle related emissions only included emissions from motor  
363 vehicles and ships, and the volatilization of fuel, while solvent usage included organic solvents volatilized from  
364 a variety of industries (the industrial produce process of electronic equipment manufacturing, furniture  
365 manufacturing, printing, packaging, inks, adhesives, etc. and other dry cleaning, catering, and architectural  
366 decoration processes). Higher vehicular emission contribution in this study may also be due to the increasing  
367 number of vehicles from 2010-2014 as a result of increased urbanization and industrialization (Statistical  
368 yearbook of Nanjing, 2014).

369  
370 Figure 5 illustrates the mean diurnal variability of all identified source at the JAES site. These trends were  
371 influenced by the variability in emission strength, mixing height, and the concentrations and photochemical  
372 reactivity of individual species in each source profile. For example, we observed a typical diurnal pattern with a  
373 broad peak between 9 am-6 pm for biogenic emissions, as the emission rate of isoprene from vegetation is largely  
374 depended on ambient temperature and sunlight intensity. Higher levels of diesel and gasoline vehicular emissions  
375 were observed in the evening and early morning due to a reduced mixing height and increased emissions from  
376 the morning and evening rush hour. Lower concentrations observed during daytime hours were likely due to  
377 decreased emissions, an increased mixing height and enhanced photochemical loss (Gillman et al., 2009; Yuan  
378 et al., 2009; Wang et al., 2013). A diurnal pattern of fuel evaporation that was similar to that of vehicular  
379 emissions. Though the evaporation of fuel is dependent on temperature, the average temperature in the morning  
380 and evening (i.e., 0800-1000 and 1700-1900 LT, respectively) when peaks of fuel evaporation were found was  
381 only about ~1.2 °C lower than that observed from noon to afternoon (1100-1600 LT), which may not result in

382 much higher fuel evaporation at noon (the difference between maximum and minimum values for fuel  
 383 evaporation was found to be  $\sim 6 \mu\text{g}/\text{m}^3$ ). On the other hand, in addition to evaporation from the gas station, fuel  
 384 could evaporate from hot engines, fuel tanks and the exhaust system when the car is running. Furthermore, the  
 385 engine remains hot for a period of time after the car is turned off, and gasoline evaporation continues when the  
 386 car is parked (Technology center, University of Illionois, <https://mste.illinois.edu/tcd/ecology/fuelevap.html>,  
 387 access date: 25 December 2019). The similarity of diurnal variations of fuel evaporation to vehicular emissions  
 388 suggested that the prominent peak in the morning and evening hours were related to the increased vehicles in  
 389 the traffic rush hour and emissions accumulated in the relatively low boundary layer. Moreover, we identified  
 390 higher concentrations of industrial emissions at night and in the early morning, with values remaining fairly  
 391 stable during daytime hours. This finding is consistent with other observations in urban and rural areas (Yuan et  
 392 al., 2009; Leuchner and Rappenglück, 2010).

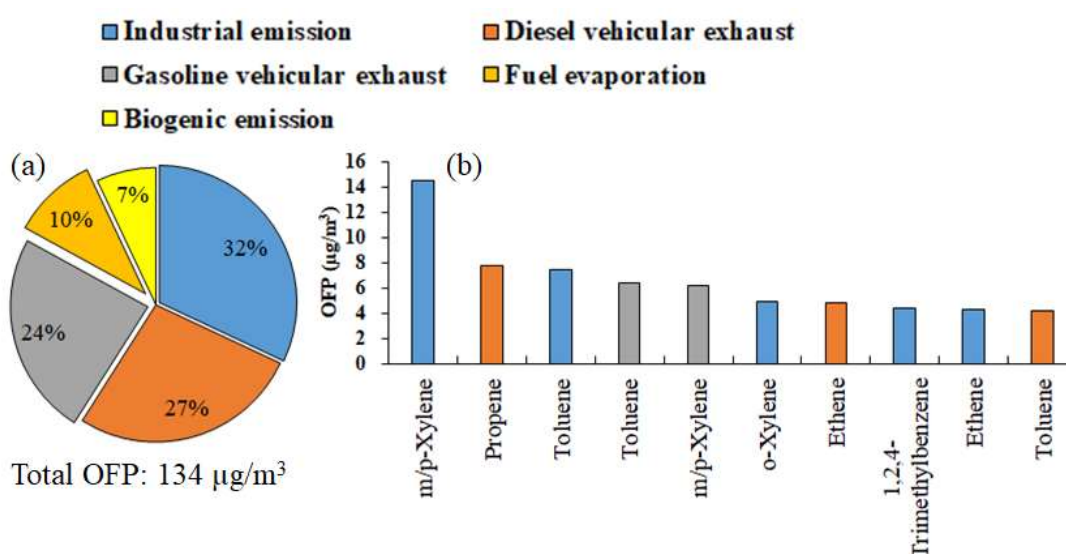


393  
 394 **Figure 5. Diurnal patterns in source concentrations of the five identified sources**

### 395 3.4 Contributions of VOC sources to O<sub>3</sub> formation

396 As important O<sub>3</sub> precursors, information on the contributions of **VOC sources** and related species to O<sub>3</sub> formation  
 397 is necessary for the formulation and implementation of VOC control measures. To achieve this goal, the  
 398 Maximum Incremental Reactivity (MIR) method, which evaluates the O<sub>3</sub> formation potential (OFP) on the basis  
 399 of mass concentrations and maximum incremental reactivities of VOCs **with the OH radical**, were adopted in  
 400 the present study (Shao et al., 2009b, 2011; Mo et al., 2017). Figure 6 presented the relative contributions of  
 401 individual VOC sources and related VOC species from PMF to OFP at the JAES site. **Industrial emissions were**  
 402 **found to have the largest OFP at JAES due to the high loadings of aromatic VOC species that have relatively**  
 403 **high OH reactivities in this source profile (Atkinson and Arey, 2003), with the OFP value of  $\sim 43 \mu\text{g}/\text{m}^3$  and the**  
 404 **contribution percentage of  $\sim 32\%$  to the total OFP of all VOC sources, followed by diesel vehicular exhausts**

405 (~36  $\mu\text{g}/\text{m}^3$ , ~27%), gasoline vehicular exhausts (~32  $\mu\text{g}/\text{m}^3$ , ~24%) and fuel evaporation (~13  $\mu\text{g}/\text{m}^3$ , ~10%).  
 406 Furthermore, though the MIR value of isoprene was much higher than other VOC species, biogenic emissions  
 407 only contributed ~7% (~9  $\mu\text{g}/\text{m}^3$ ) to the total OFP of all VOC sources as the relatively low mixing ratio of  
 408 isoprene at the JAES site. Similarly, using the same method to evaluate OFP of different VOC sources, Mo et al.  
 409 (2017) found that industrial emissions (including the emissions of petrochemical industry, chemical and paint  
 410 industries, solvent usage) and vehicular emissions were the dominant VOC sources of the total OFP in an  
 411 industrialized coastal city (i.e., Ningbo) in the YRD region. Therefore, our results further demonstrated the need  
 412 to minimize VOC emissions from industrial emissions and vehicle exhausts in order to lower  $\text{O}_3$  formation and  
 413 photochemical pollution in YRD.



414  
 415 **Figure 6. (a) The contribution of individual sources to the total OFP of all sources extracted from PMF and (b) OFP values**  
 416 **of the top 10 VOC species in the different source categories.**

417  
 418 Based on the mass concentrations of individual species in each source, we found that *m,p*-xylene and toluene in  
 419 industrial emissions and gasoline vehicular emissions, propene, ethene, toluene and *m,p*-xylene in diesel  
 420 vehicular emissions, and *o*-xylene, 1,2,4-trimethylbenzene and ethene in industrial emissions to be the dominant  
 421 species from VOC emissions contributing to photochemical  $\text{O}_3$  formation. Thus, only a small number of VOC  
 422 species can be monitored for the effective control of  $\text{O}_3$  formation.

### 423 424 3.5 Policy summary and implications

425 To effectively control photochemical pollution, the Prevention and Control of Atmospheric Pollution Act was  
 426 passed in 1987 and amended in 2015. As a result, a series of measures to prevent and control VOCs levels have  
 427 been and are being implemented by central and local governments, including the implementation of new laws  
 428 and regulations, and the advancement of technology. The results of this study suggest that photochemical  $\text{O}_3$



429 formation within the urban areas of Nanjing city are VOC-limited, which is consistent with observations in the  
430 urban locations of other regions, including the North China Plain, the Yangtze River Delta and the Pearl River  
431 Delta. Minimizing VOC emissions and their concentrations should therefore be prioritized in order to alleviate  
432 O<sub>3</sub> pollution in urban environments. The prevention and control of VOC pollution has been listed as one of the  
433 key tasks of “the Blue Sky” Project initiated in 2012 by the Department of Environmental Protection of Jiangsu  
434 Province. Furthermore, the administrative measures on the Prevention and Control of Volatile Organic  
435 Compounds Pollution in Jiangsu (Order No. 119 of the Provincial Government) was enacted on March 6, 2018  
436 and implemented on May 1, 2018, with the aim of controlling VOC emissions in Jiangsu Province.

437  
438 In order to achieve these goals, various measures have been implemented (Table S2), including: 1) investigating  
439 the current pollution status and identifying the progress of VOC prevention and control in Jiangsu Province  
440 (Provincial Office of the Joint Conference on the prevention and control of air pollution [2012] No. 2); 2)  
441 conducting a strict industry access system, under the Advice on Promoting Air Pollution Joint Prevention and  
442 Control Work to Improve Regional Air Quality (Office of the State Council [2010] No. 33); 3) strengthening the  
443 remediation on existing sources of VOCs and reducing VOC emissions from these sources, under the Guidelines  
444 for the Implementation of Leak Detection and Repair (LDAR) in Jiangsu Province (Trial) (Provincial Office of  
445 Environmental Protection [2013] No. 318); 4) strengthening the VOC monitoring capacity, under the Guidelines  
446 for Control of Volatile Organic Compounds Pollution in Key Industries in Jiangsu Province (Provincial Office  
447 of Environmental Protection [2013] No. 128); 5) improving standards regarding VOC emissions for key  
448 industries, including standards for surface coating of the automobile manufacturing industry (DB32/2862-2016),  
449 the chemical industry (DB32/3151-2016), and furniture manufacturing operations (DB32/3152-2016), which are  
450 still effective since their enforcement; 6) implementing the Pilot Measures for Volatile Organic Compounds  
451 Discharge Charges (Ministry of Finance [2015] No. 71) on October 1, 2015 to raise awareness pertaining to  
452 emissions reduction in factories and to control VOC emissions from industrial sources; 7) encouraging the public  
453 to live a low-carbon life and supervise and offer recommendations in accordance with the laws, under the  
454 Measures for Public Participation in Environmental Protection in Jiangsu Province (Trial) (Provincial Regulation  
455 of Environmental Protection Office [2016] No. 1).

456  
457 Based on the VOC source apportionment results in this study, we identified vehicular emissions and industrial  
458 emissions as the two major VOC sources contributing to photochemical O<sub>3</sub> formation. Other measures and/or  
459 regulations have been conducted in the Jiangsu Province to effectively control VOC emissions from vehicles  
460 and industry. For vehicular emissions, the Regulations on Prevention and Control of Vehicle Exhaust Pollution  
461 in Nanjing was amended in July 2017, and subsequently in March, 2018  
462 (<http://hbt.jiangsu.gov.cn/col/col11590/index.html>). The new regulation not only focusses on vehicle emissions,  
463 but also incorporates a number of additional topics, including optimizing the function and distribution of urban  
464 areas, limiting the number of vehicles in the region, promoting new green energy vehicles, and improving the



465 quality of fuel. The promotion of intelligent traffic management, implementation of a priority strategy for public  
466 transportation, and construction of more efficient traffic systems to promote pedestrian and bicycle use is  
467 recommended. Further studies should be conducted to estimate and manage the increasing quantity of vehicles  
468 on the road. As of January 1, 2017, regulation stipulate that all new and used vehicles should meet the fifth phase  
469 of vehicle emission standards, including vehicle manufacture, sales, registration and importation. For vehicles  
470 already in use, an environmental protection examination should be conducted annually, based on the standards  
471 of GB 14622-2016, GB 18176-2016, GB 19755-2016, and HJ 689-2014. Penalties are issued if qualified  
472 vehicles excessively emit pollutants due to poor maintenance.

473  
474 For industrial emissions, various policies have been implemented to reduce VOC emissions, particularly in  
475 chemical industries: including, 1) investigations on the VOC emissions of the chemical industry and the  
476 establishment of an archive system for VOC pollution control, particularly the inspection of industry information,  
477 products and materials, unorganized emission of storage and exhaust gas treatment facilities, under the Plan for  
478 Investigation of Volatile Organic Pollutant Emissions in Jiangsu Province, mentioned in the Provincial Office of  
479 Environmental Protection [2012] No. 183; 2) exhaust gas remediation in the chemical industry park, under the  
480 Technical Specifications for Prevention and Control of Air Pollution in Chemical Industries in Jiangsu Province  
481 (Provincial Office of Environmental Protection [2014] No. 3), which requires the establishment of the long-term  
482 supervision of exhaust gas remediation in the chemical industry park of Jiangsu Province; 3) a pilot project on  
483 the leak detection and repair (LDAR) technology in the chemical industry park, under the notification on carrying  
484 out the technical demonstration and pilot work of leak detection and repair (LDAR) in petrochemical and  
485 chemical industries (Provincial Office of Environmental Protection [2015] No. 157). The TVOC removal  
486 efficiency of organic exhaust vents should be >95%, and higher for areas of excessive environmental pollution  
487 at >97% (GB 31571-2015).

488  
489 Furthermore, though measures have been adopted to improve standards and control vehicle VOC emissions,  
490 most of these policies only focus on total VOC emissions (or the mass of total emissions) and do not consider  
491 the impacts of individual VOC species. To accelerate the implementation of existing policies and to strengthen  
492 collaborative regional prevention and control, priority should be placed on specific high-impact VOC species  
493 (i.e., *m,p*-xylene and toluene in the industrial emission and gasoline vehicular emission) by considering both  
494 their reactivity and abundance.

495  
496 Last but not the least, O<sub>3</sub> pollution is a regional cross-boundary environmental issue rather than a local pollution  
497 problem. Apart from VOCs, NO<sub>x</sub> was another important precursor for O<sub>3</sub> formation with its dual roles in O<sub>3</sub>  
498 production (enhancing O<sub>3</sub> formation in non NO<sub>x</sub>-saturated environment and titrating O<sub>3</sub> in NO<sub>x</sub>-saturated  
499 environment). In other areas (i.e., the rural environment and/or the downwind areas of urban center in the same  
500 region) where the concentrations of NO<sub>x</sub> are low and/or there is a non NO<sub>x</sub>-saturated environment, the situation

501 may be different and controlling VOCs should be conducted cautiously (Zheng et al., 2010; Yuan et al., 2013;  
502 Ou, et al., 2016). Therefore, from a regional perspective, the benefits of VOCs control measures could be further  
503 evaluated with those of  $\text{NO}_x$  (i.e., the appropriate ratios of  $\text{VOC}/\text{NO}_x$  for the reduction of  $\text{O}_3$  pollution) as well  
504 as the associated  $\text{O}_3$ -VOCs- $\text{NO}_x$  sensitivity. Therefore, one important concern for the policy formulation and  
505 implementation system is whether controlling VOCs and  $\text{NO}_x$  individually or controlling both VOCs and  $\text{NO}_x$   
506 is more effective and appropriate for alleviating  $\text{O}_3$  pollution. It is necessary to consider the reduction ratios of  
507  $\text{VOC}/\text{NO}_x$  when VOCs and  $\text{NO}_x$  are simultaneously controlled. Finally, long-term monitoring studies are  
508 necessary to determine the cost-benefits and performance of each policy.

#### 509 **4. Conclusion**

510 In this study, a one-year field sampling campaign was conducted to investigate the VOC characteristics at an  
511 urban site in Nanjing (the JAES site), Jiangsu province. In total, 56 VOCs including 29 alkanes, 10 alkenes, 16  
512 aromatics and acetylene were identified and quantified. The composition analysis found that alkanes were the  
513 dominant group of VOCs observed at the JAES site (~53%), followed by aromatics, acetylene, and alkenes. This  
514 finding is consistent with the VOC measurements in studies conducted in the North China Plain, Pearl River  
515 Delta, and Yangtze River Delta. We observed distinct seasonal patterns of TVOCs, with maximum values in  
516 winter and minimum values in summer. Similarly, prominent morning and evening peaks were observed in the  
517 diurnal variability of TVOCs, influenced by local emissions and meteorology.

518  
519 Based on the observed VOC data, we identified five dominant VOC sources at the JAES site using a PMF model.  
520 By considering both the abundance and maximum incremental reactivity of individual VOC species in each  
521 source, the OFP values identified industrial and vehicular emissions, particularly *m,p*-xylene, toluene and  
522 propene, as the main contributors of  $\text{O}_3$  pollution. Local governments have strengthened several measures to  
523 minimize VOC pollution from vehicle and industrial emissions in the Jiangsu province in recent years, though  
524 most of these policies focus particularly on lowering the total emissions of VOCs. Furthermore, from a regional  
525 perspective, it is suggested that appropriate ratios of  $\text{VOC}/\text{NO}_x$ , their associated sensitivity to  $\text{O}_3$  formation and  
526 relative benefits/disbenefits of reducing  $\text{VOCs}/\text{NO}_x$  should be investigated and evaluated when control measures  
527 of VOCs and  $\text{NO}_x$  were both conducted.

528

529 **Author Contributions.** Jun Bi, Zhenhao Ling, and Qiuyue Zhao designed the research and carried them out.  
530 Zhenhao Ling performed the data simulation. Qiuyue Zhao and Guofeng Shen performed the observation data  
531 analysis. Qiuyue Zhao prepared the manuscript with contributions from all co-authors.

532 **Competing Interests.** The authors declare that they have no conflict of interest.

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