

# VOC species and emission inventory from vehicles and their SOA formation potentials estimation in Shanghai, China

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**Abstract:** VOC species from vehicle exhaust and gas evaporation were investigated by chassis dynamometer and on-road measurements of 9 gasoline vehicles, 7 diesel vehicles, 5 motorcycles, and 4 gas evaporation samples. The SOA mass yields of gasoline, diesel, motorcycle exhausts, and gas evaporation were estimated based on the mixing ratio of measured C<sub>2</sub>-C<sub>12</sub> VOC species and references IVOC species. High aromatic contents were measured in gasoline exhaust and contributed more SOA yield comparatively. A vehicular emission inventory was compiled based on a local survey of on-road traffic in Shanghai and real-world measurements of vehicle emission factors from previous studies in the cities of China. The inventory-based vehicular OA productions to total CO emissions were compared with the observed  $\Delta\text{OA}/\Delta\text{CO}$  in the urban atmosphere. The results indicate that vehicles dominate the POA emissions and OA productions, which contributed about 40% and 60% of OA mass in the urban atmosphere of Shanghai. Diesel vehicles, which accounted for less than 20% of VKT, contribute more than 90% of vehicular POA emissions and 80%-90% of OA mass derived by vehicles in urban Shanghai. Gasoline exhaust could be an important source of SOA formation. Tightening the limit of aromatic content in gasoline fuel will be helpful to reduce its SOA contribution. IVOCs in vehicle exhausts have great contributions to SOA formation in the urban atmosphere of China.

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27 However, more experiments need to be conducted to determine the contributions of  
28 IVOCs to OA pollution in China.

29 **Key words:** SOA; VOC species; vehicle emission; emission inventory; organic  
30 aerosol

### 31 **1. Introduction**

32 Secondary organic aerosol (SOA) accounts for a significant fraction of ambient  
33 tropospheric aerosol (Hallquist et al., 2009; Jimenez et al., 2009). De Gouw and  
34 Jimenez (2009) suggested that SOA from urban sources may be the dominant source  
35 of organic aerosol globally between 30 and 50 latitude.

36 Gas-phase oxidation of volatile organic compounds (VOCs) has traditionally  
37 been considered to be the major source of urban SOA formation. VOCs are oxidized  
38 to low vapor pressure reaction products by OH radical, ozone, and NO<sub>3</sub> radical, and  
39 eventually form organic aerosol (OA) in the atmosphere. Odum et al. (1997)  
40 investigated the SOA formation from vaporized reformulated gasoline and found  
41 single light aromatic hydrocarbons are responsible for the majority of SOA formation.  
42 Kleindienst et al. (2002) verified that 75–85% of the SOA was due to reaction  
43 products of C6-C9 light aromatic compounds from automobile exhaust. Robinson et  
44 al. (2007) further recognized that intermediate-volatile organic compounds (IVOCs)  
45 and semi-volatile organic compounds (SVOCs) are also important sources for OA  
46 production based on the smog chamber studies of diesel exhaust and wood fire  
47 (Weitkamp et al., 2007; Grieshop et al., 2009). Their subsequent study pointed IVOCs  
48 such as long-chain and branched alkanes from vehicle exhaust play more important  
49 roles in SOA production compared with other combustion emissions (Jathar et al.,  
50 2013). A recent study from Zhao et al. (2014) concluded that primary IVOCs were  
51 estimated to produce about 30% of newly formed SOA in the afternoon during  
52 CalNex campaign in Pasadena, California.

53 Due to the abundance of reactive organic compounds, vehicle emission has been  
54 recognized as a major source of urban SOA formation (Stone et al., 2009; Liu et al.,

55 2012; Borbon et al., 2013). Laboratory chamber studies also report significant SOA  
56 production from diesel, gasoline, and motorcycle exhaust photo-oxidation (Hung et al.,  
57 2006; Weitkamp et al., 2007; Chirico et al., 2010; Nordin et al., 2013; Platt et al.,  
58 2013). Current research is now focusing on the relative importance of gasoline and  
59 diesel vehicles to urban SOA formation. Bahreini et al. (2012) and Hayes et al. (2013)  
60 suggested gasoline emissions dominate over diesel in urban SOA formation by field  
61 studies. Gentner et al. (2012) argued diesel is responsible for 65% to 90% of  
62 vehicular-derived SOA based on the estimation of SOA formation from gasoline and  
63 diesel fuel compositions.

64 Shanghai is one of the most urbanized cities in the Yangtze River Delta (YRD)  
65 region in China. The YRD region occupies 2% of land area and generates 8%-12% of  
66 the primary PM<sub>2.5</sub> and the emissions of its precursors in China (Huang et al., 2011).  
67 Motor vehicles are the fastest growing source of pollution in the megacities of China.  
68 The number of vehicles in Shanghai was doubled in the last decade and reached 2.6  
69 million (about 107 units per 1000 capita) in 2012 (SCCTPI, 2013). Gasoline and  
70 diesel vehicles increased by 2.8 and 1.3 times, respectively, while motorcycle  
71 decreased by 36%. Vehicular emission has been recognized as the largest source of  
72 VOCs in urban Shanghai, which contributes 25%~28% of the measured VOC  
73 concentrations. Other VOC emission sources were solvent usage, chemical industry,  
74 petrochemical industry, and coal burning, etc. (Cai et al., 2010; Wang et al., 2013).  
75 Yuan et al. (2013) indicated that VOC emissions are large contributors to SOA  
76 formation through field measurements at a receptor site in eastern China. Huang et al.  
77 (2012, 2013) reported that 28.7%-32.1% of the fine particle mass is organic matter  
78 (OM) and 30.2%-76% of OM is contributed by SOA in the atmosphere of Shanghai  
79 and its surrounding areas. Based on the historical measurement data of organic (OC)  
80 and element carbon (EC) in PM<sub>2.5</sub> in the atmosphere in urban Shanghai, the OC/EC  
81 ratio shows growing trend from 1999 to 2011, which implies that the secondary  
82 fraction of organic matter is playing an increasing role in urban Shanghai (Ye et al.,

83 2003; Feng et al., 2005; Hou et al., 2011; Cao et al., 2013; Feng et al., 2013).  
84 However, the contribution of VOC emissions to SOA formation and the relative  
85 importance of vehicular emission remain unclear. At present, vehicle use is  
86 experiencing a rapid growth episode in the cities of China. Understanding the  
87 contribution of vehicular VOC emissions to SOA formation will be helpful to identify  
88 the source of OA and PM<sub>2.5</sub> pollution in China.

89 In this study, we first constructed a vehicular emission inventory of Shanghai for  
90 the year of 2012. Then the SOA yields of VOCs emissions from different vehicle  
91 types were discussed based on the new measurements of VOCs species from a fleet of  
92 vehicles in Shanghai. Finally, we calculated the inventory-based vehicular OA  
93 production with the ambient observation data to evaluate the OA contribution of  
94 vehicle emission. The main purpose of this study is to discuss: (1) the contribution of  
95 vehicle emission to OA in urban Shanghai; (2) the relative contributions of gasoline  
96 and diesel vehicles to vehicle derived OA.

## 97 **2. Materials and methods**

### 98 2.1 Vehicular emission inventory establishment

#### 99 2.1.1 Methodology of emission inventory compilation

100 We developed emission inventories for the pollutants including VOCs, CO, EC,  
101 and OC with the IVE (International Vehicle Emission) model for Shanghai, China.  
102 The methodology of the model has been introduced by Wang et al. (2008). Vehicle  
103 kilometers of travel (VKT), vehicle flow distribution, driving pattern, fleet  
104 composition and emission factor of each vehicle type were 5 key parameters for the  
105 development of vehicle emission inventory. Vehicle emissions can be calculated with  
106 Eq. (1).

$$107 \quad E = \sum_t \{ VKT \times f_{[t]} \times EF_{[t]} \times \sum_d [f_{[dt]} \times K_{[dt]}] \} \quad (1)$$

108 Where,  $E$  is emission amount of each vehicle type (g).  $VKT$  is Vehicle kilometers of  
109 travel of each vehicle type (km).  $f_{[ij]}$  is the fleet composition of the specific technology

110 of each vehicle type (%), such as fuel type, engine size, and emission standard.  $EF_{[ij]}$   
111 is the emission factor of each vehicle technology ( $\text{g}\cdot\text{km}^{-1}$ ).  $f_{[dt]}$  is the fraction of the  
112 driving pattern (%).  $K_{[dt]}$  is the correction factor of each driving pattern determined by  
113 the model (unitless). Evaporative emissions are also calculated with Eq. (1).  $EF_{[ij]}$  will  
114 be evaporative emission factor of each vehicle technology as the evaporative  
115 emissions are calculated.

### 116 2.1.2 Road traffic data survey

117 VKTs and their weights on 3 road types (including highway, arterial road, and  
118 residential road) were surveyed from transportation for the year of 2012. VKTs on  
119 each road type were further separated into 7 vehicle types by the use of video camera  
120 surveys. The distributions of each vehicle type were surveyed on various road types  
121 with video cameras from March to May. About 4000 valid hours were obtained on 15  
122 roads covering 3 road types. Survey days included weekdays and weekends and each  
123 day covered 24 h. The results show that light-duty vehicles (including light-duty cars,  
124 light-duty trucks, and taxis) are the major vehicle types on the road, accounting for  
125 56% of the total flows. Heavy-duty vehicles (including heavy-duty bus, heavy-duty  
126 truck, and city bus) comprise 19% of the whole VKTs in Shanghai. GPS data were  
127 used to determine the driving patterns of various vehicle types. The driving patterns  
128 were determined by the average speeds and VSP (Vehicle Specific Power)  
129 distributions. We installed GPS units on light-duty cars, taxis, buses, and heavy-duty  
130 trucks to record the driving speeds and altitudes second by second. About 150 hours  
131 of valid GPS data were collected in this study. The data covered 2831 km of roads and  
132 were composed of 3 road types and 4 vehicle types. VSP of each vehicle and road  
133 type can be calculated with Eq. (2) introduced by Jimenez (1999).

$$134 \quad VSP(kW \cdot t^{-1}) = v \times [1.1a + 9.81 \times (a \cdot \tan(\sin(\text{grade}))) + 0.132] + 0.000302 \times v^3 \quad (2)$$

135 Where,  $v$  is vehicle speed ( $\text{m}\cdot\text{s}^{-1}$ ).  $a$  is vehicle acceleration ( $\text{m}\cdot\text{s}^{-2}$ ).  $\text{grade}$  is vertical  
136 rise/slope length. Table 1 shows the daily VKT and average speeds of various vehicle  
137 and road types in 2012.

### 138 2.1.3 Fleet composition data survey

139 Fleet composition data were used to separate the VKT of each vehicle type (as  
140 shown in Table 1) into the fractions of specific technologies, such as fuel type, engine  
141 size, and emission standard. The data were determined by the ratios of the populations  
142 of specific technologies in the vehicle information database from the Vehicle  
143 Management Department of Public Security Bureau of Shanghai. We call this “static”  
144 fleet. Light-duty cars and taxis were mainly composed of gasoline vehicles, which  
145 occupied 98% and 97%, respectively. Diesel vehicles dominated in light-duty truck,  
146 heavy-duty bus, heavy-duty truck, and city bus, comprising 56%, 91%, 89%, and 98%,  
147 respectively. Euro 2 vehicles were the majority of light-duty cars and light-duty trucks,  
148 accounting for 51% and 68%, respectively. Heavy-duty buses and trucks were mainly  
149 composed of Euro 2 and Euro 3 diesel vehicles, which comprised 40% and 45% of  
150 each vehicle type. However, the fraction of each specific technology should be  
151 changed with its occurrence frequency in the real-world. Generally, older vehicles  
152 show less occurrence frequency than newer vehicles, which means the annual mileage  
153 of older vehicle should be less than the newer one. For this reason, we considered to  
154 adjust the fleet compositions according to their real-world annual average mileages.  
155 About 30,000 vehicles were surveyed at 4 inspection stations in this study. Vehicle  
156 age and odometer reading were recorded for each vehicle. The survey data showed  
157 that the annual average mileages of light-duty truck, heavy-duty bus, and heavy-duty  
158 truck tended to decrease with the increase of their vehicle ages. The “adjusted” fleet  
159 compositions were determined by the multiplication of vehicle populations and their  
160 surveyed annual mileages. Fig. 1 shows the static and adjusted fraction by each  
161 vehicle type in Shanghai. It is indicated that the adjusted fractions of the older  
162 vehicles with pre-Euro and Euro 1 emission standard for light-duty truck, heavy-duty  
163 bus, heavy-duty truck, and city bus were much lower than those of the static ones.  
164 Correspondingly, the adjusted fractions of the newer vehicles with Euro 3 emission  
165 standard increased a lot compare with the static ones.

#### 166 2.1.4 Vehicle emission factors

167 The emission factors of each vehicle technology were modeled with the IVE  
168 model. However, most of the default emission factors in the model are based on the  
169 measurements in the US. To localize the emission factors in this study, we collected  
170 the published emission factors based on the real-world measurements in the previous  
171 studies to adjust the modeled emission factors. The measurements were all conducted  
172 with Portable Emission Measurement Systems (PEMS) under designed driving routes  
173 in the cities of China. The cities included Shanghai, Beijing, Guangzhou, Xi'an,  
174 Shenzhen, Jinan, and Yichang (Chen et al., 2007; Huo et al., 2012a; Huo et al., 2012b;  
175 Wu et al., 2012; Huang et al., 2013). Fig. 2 shows the comparisons of the adjusted  
176 emission factors with the measured ones. The evaporative emission factors were not  
177 adjusted due to the lack of measurement data. Default factors in the model were used  
178 to calculate evaporative emissions in this study. It is indicated that the adjusted  
179 emission factors of each vehicle type generally fit well with the measured results. The  
180 emission factors are reliable to be used to establish the emission inventory.

#### 181 2.2 VOC species measurements and SOA yield estimation

##### 182 2.2.1 VOC sampling

183 The exhaust from 4 light-duty gasoline vehicles (LDGVs), 5 taxis, 5 heavy-duty  
184 diesel trucks (HDDTs), 2 city buses (buses), and 5 motorcycles (MTs) were measured  
185 in June 2010. LDGVs, taxis, and MTs were fueled by gasoline. HDDTs and buses  
186 were fueled by diesel. The emission standards of the tested vehicles covered Euro 1 to  
187 Euro 3 and their model years covered 2001 to 2009. All MTs were 4-stroke with 125  
188 cc displacement and without catalytic converter or any other pollution control device.  
189 All gasoline vehicles were equipped with catalytic converters. Diesel vehicles didn't  
190 install any aftertreatment device like DPF (Diesel Particle Filter). Table 2 lists the  
191 detailed information of the tested vehicles. Commercially available fuels were used in  
192 the test. The fuel quality met the requirements of the local standard in Shanghai. The  
193 sulfur contents of both gasoline and diesel fuel were below 50 ppm.

194 All the automobiles were measured on chassis dynamometers. LDGVs and taxis  
195 were measured utilizing a vehicle mass analysis system (VMAS), which was widely  
196 used in in-use vehicle inspection stations in China. VOC sample was collected from a  
197 1-bag test of the Economic Commission of Europe (ECE) urban cycle. The highest  
198 speed reaches  $50 \text{ km}\cdot\text{h}^{-1}$  and the average speed is about  $18.8 \text{ km}\cdot\text{h}^{-1}$ . HDDTs and  
199 buses were measured on a loaded mode test cycle. The tested vehicles were operated  
200 on idling and a test cycle which simulates high engine loads under 100%, 90%, and  
201 80% of their maximum powers. The highest speed reaches  $70 \text{ km}\cdot\text{h}^{-1}$ . MT exhausts  
202 were sampled while operating on the road. A GPS unit was installed on the tested  
203 motorcycles to record the speeds second by second. The highest speed reached  $50$   
204  $\text{km}\cdot\text{h}^{-1}$  and the average speed was about  $20 \text{ km}\cdot\text{h}^{-1}$ . Vehicle exhaust was sampled into  
205 a Summa canister (Entech Inst., USA) during the whole driving cycle. We also  
206 collected the samples of gasoline vapor at 4 gas stations in Shanghai to analyze the  
207 VOC species of non-tailpipe gasoline.

#### 208 2.2.2 VOC analysis

209 Concentration of C2-C12 VOCs in samples were determined by a GC-MS  
210 system (Agilent 7890A/5975C) with standard gases prepared by Spectra Gas. The  
211 samples collected in the Summa canister were pre-concentrated to an acceptable level  
212 for the analytical devices using a 7100A pre-concentrator (Entech Inst., USA) with an  
213 Entech 7016CA automatic sample injector. A 50 mL sample was extracted by the  
214 pre-concentrator into a 1/4 inch liquid nitrogen cold trap to remove water and  $\text{CO}_2$ ,  
215 and then separated by GC and detected by MS. The carrier gas was helium.

#### 216 2.2.3 SOA yield estimation

217 To investigate the SOA formation potentials of VOC emissions in vehicle  
218 exhausts and gas evaporation, we calculated the SOA yields of the exhausts from  
219 gasoline, diesel, and motorcycle vehicles and evaporative emissions with the  
220 following equation.



221 
$$Y_j = \frac{\sum (C_{i,j} \times Y_i)}{\sum VOC_j} \quad (3)$$

222 Where,  $Y_j$  is the SOA yield of source  $j$  (unitless).  $C_{ij}$  is the weight percent (by carbon)  
223 of species  $i$  in which can be identified by measurements or references from source  $j$   
224 (wtC%).  $VOC_j$  is the weight percent (by carbon) of total identified SOA precursors  
225 and unidentified species. Identified non-SOA precursors were excluded from total  
226 VOC emissions. The weight percentages of identified species were determined by the  
227 measurements above. The unidentified species accounted for about 25%, 60%, and  
228 50% in gasoline, diesel, and motorcycle exhausts, respectively. Considering IVOCs  
229 which had high SOA formation potentials were not measured in this study, we  
230 combined the amounts of alkanes and aromatics larger than C12 and polycyclic  
231 aromatics from Gentner et al. (2012) with the identified species to compare the  
232 differences of SOA yields with or without IVOCs.  $Y_i$  is the yield of species  $i$  under  
233 high-NOx condition considering the study was focusing on urban area with high NOx  
234 concentration (unitless). The yield for each SOA precursor was referenced from  
235 Gentner et al. (2012), which listed the yields of known and estimated compounds  
236 using a combination of measured SOA yields derived from laboratory-chamber  
237 experiments and approximate SOA yields based on box modeling.

## 238 2.3 Air pollution observation and vehicular OA contribution determination

### 239 2.3.1 Air pollution observation

240 To estimate the vehicular OA production in the atmosphere, we calculated the  
241 SOA formation potentials from vehicular VOC emissions based on observation data  
242 with a photochemical- age-based parameterization method. The observation data were  
243 obtained from a monitoring site on the roof of a 5-floor building (15 m high above the  
244 ground) at Shanghai Academy of Environmental Science (31.17°N, 121.43°E), which  
245 was located southwest of urban area of Shanghai. The site was mostly surrounded by  
246 commercial properties and residential dwellings. Vehicle exhaust was a major source  
247 of pollutants near this site. Fig. S1 shows the location of monitoring site in this study.

248 Carbon monoxide was continuously measured by an ECOTECH EC9820 CO analyzer.  
 249 PM<sub>2.5</sub> concentration was measured by a Thermo Fisher commercial instrument  $\beta$ -ray  
 250 particulate monitor. Organic carbon (OC) and elemental carbon (EC) were measured  
 251 by a carbon analyzer (model RT-4, Sunset Laboratory Inc.). Water soluble ions were  
 252 measured by a commercial instrument for online monitoring of aerosols and gases  
 253 (MARGA, model ADI 2080, Applikon Analytical B.V.). Individual VOC species were  
 254 continuously measured every 30 minutes by two on-line gas chromatographs with  
 255 flame ionization detector (GC-FID) systems (Chromato-sud airmoVOC C2–C6  
 256 #5250308 and airmoVOC C6–C12 #2260308, France). Fig. S2 shows the time series  
 257 data of meteorological parameters and concentrations of major air pollutants observed  
 258 in urban Shanghai in summer (August in 2013) and winter (January in 2013). We  
 259 didn't measure the OA concentration due to the lack of observation equipment. The  
 260 OA concentrations were determined by OC concentrations multiplying the OM/OC  
 261 ratio. Turpin et al. (2001) suggested a ratio around 1.2-1.6 from fresh emission to aged  
 262 air mass in remote area. Considering our study was mainly focusing on urban area  
 263 where emissions were not fully aged, we used the ratio of 1.4 to convert OC  
 264 concentrations.

### 265 2.3.2 OA production estimation

266 The evolution of primary VOC emissions to SOA formation is determined by  
 267 OH exposure in the atmosphere. The OH exposure can be calculated with Eq. (4)  
 268 developed by de Gouw et al. (2005, 2008).

$$269 \quad \Delta t \cdot [OH] = \frac{1}{(k_X - k_E)} \times \left[ \ln \left( \frac{[X]}{[E]} \right)_{t=0} \right] - \ln \left( \frac{[X]}{[E]} \right) \quad (4)$$

270 Here,  $\Delta t$  is photochemical age (h).  $[OH]$  is the average OH radical concentrations  
 271 (molecules·cm<sup>-3</sup>). The ratio of m,p-xylene to ethylbenzene (X/E) was considered as a  
 272 photochemical clock.  $k_X$  and  $k_E$  are the OH rate constants of m,p-xylene ( $18.9 \times 10^{-12}$   
 273 cm<sup>3</sup>·molecule<sup>-1</sup>·s<sup>-1</sup>) and ethylbenzene ( $7.0 \times 10^{-12}$  cm<sup>3</sup>·molecule<sup>-1</sup>·s<sup>-1</sup>) (Yuan et al.,  
 274 2013).  $[X]/[E]_{t=0}$  and  $[X]/[E]$  are initial emission ratio and the ratio after

275 photochemical reaction of m,p-xylene to ethylbenzene. The concentrations of  
 276 m,p-xylene and ethylbenzene showed good correlations during the observation (Fig.  
 277 S3). The different diurnal variations of m,p-xylene and ethylbenzene indicated that  
 278 they are engaged in different chemical reactions in the daytime (Fig. S4). Fig. 3  
 279 illustrates the diurnal distributions of the ratios of observed m,p-xylene to  
 280 ethylbenzene in summer and winter of 2013. The initial emission ratios of m,p-xylene  
 281 to ethylbenzene were determined by the X/E ratio on 97.5 percentiles, which were  
 282 2.17 and 1.68 in summer and winter, respectively.

283 OA production is determined by the loss terms and formation rates of OA  
 284 concentration after POA emissions exhaust into the atmosphere. de Gouw et al. (2008)  
 285 introduced a method to explain the OA evolution during photochemical aging of  
 286 urban plumes as shown by Eq. (5).

$$\begin{aligned}
 \frac{\Delta OA}{\Delta CO} &= \frac{\Delta POA}{\Delta CO} + \frac{\Delta SOA}{\Delta CO} \\
 &= ER_{POA} \times \exp(-L_{OA} \cdot \Delta t) + ER_{VOC_j} \times Y_j \times \frac{P_{OA}}{L_{OA} - P_{OA}} \times [\exp(-P_{OA} \cdot \Delta t) - \exp(-L_{OA} \cdot \Delta t)]
 \end{aligned}
 \tag{5}$$

288 Here,  $\Delta OA/\Delta CO$  is the ratio of OA formation versus CO emission after photochemical  
 289 reaction ( $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$ ).  $ER_{POA}$  is the primary emission ratio of OA to CO emission  
 290 ( $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$ ).  $ER_{VOC_j}$  is the primary emission ratios of VOC (including SOA  
 291 precursors and unidentified species) from source  $j$  to CO emission in the unit of  
 292  $\text{ppbv}^{-1}\cdot\text{ppmv}^{-1}$ .  $Y_j$  is the SOA yield of source  $j$ , which is determined by Eq. (3).  $L_{OA}$   
 293 and  $P_{OA}$  are the loss and formation rate of organic aerosol, respectively. We used the  
 294 empirical parameters derived by de Gouw et al. (2008), which were  $0.00677\text{ h}^{-1}$  and  
 295  $0.0384\text{ h}^{-1}$ , respectively.  $\Delta t$  is the photochemical age calculated by equation (4).  
 296 Because there is no OH measurement in Shanghai, we reference the 24-h average OH  
 297 concentration ( $3\times 10^6\text{ molecules}\cdot\text{cm}^{-3}$ ) from de Gouw et al. (2008).

### 298 2.3.3 Determination of vehicular OA contribution

299 The observed  $\Delta OA/\Delta CO$  in the atmosphere represents the ratio of total POA  
 300 emissions and their SOA formation to total CO emissions from all sources, which can  
 301 be explained by Eq. (6) as follows.

$$302 \quad \left( \frac{\Delta OA}{\Delta CO} \right)_{obs} = \frac{POA_{total} + SOA_{total}}{CO_{total}} = \frac{(POA_{veh} + SOA_{veh})}{CO_{total}} + \frac{(POA_{oth} + SOA_{oth})}{CO_{total}} = \frac{OA_{veh}}{CO_{total}} + \frac{OA_{oth}}{CO_{total}} \quad (6)$$

303 The contribution of vehicular OA to total OA production in the atmosphere can be  
 304 determined by the ratio of  $OA_{veh}/CO_{total}$  to  $(\Delta OA/\Delta CO)_{obs}$ . Here,  $(\Delta OA/\Delta CO)_{obs}$  is the  
 305 ratio of observed  $\Delta OA$  (Obs,  $OA - OA_{background}$ ) to observed  $\Delta CO$  (Obs,  
 306  $CO - CO_{background}$ ) in the unit of  $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ .  $OA_{veh}/CO_{total}$  is the ratio of vehicular  
 307 POA emission and SOA formation to total CO emissions, which can be calculated by  
 308 Eq. (5).  $ER_{POA}$  and  $ER_{VOCj}$  in Eq. (5) should be substituted by the ratios of vehicular  
 309 POA and VOC emissions to total CO emissions from vehicle and other sources. The  
 310 total amount of CO emission was  $1.2 \times 10^6$  tons according to the annually updated  
 311 emission inventory in Shanghai for the year of 2012. Iron & steel manufacturing was  
 312 the major source of CO emission, which accounted for 54% of the total. The sector  
 313 produced  $19.7 \times 10^6$  and  $18 \times 10^6$  tons of pig irons and crude steels, and consumed more  
 314 than  $10 \times 10^6$  tons of coal in 2012. Vehicles were the second largest source, accounting  
 315 for 27.8% of the total. Detailed information is shown in Fig. S5. However,  
 316 considering the observation site was located in the urban area and most of the large  
 317 CO emission sources were located at the surrounding areas (about 30-50 km from city  
 318 center), it would be more reasonable to exclude the emissions out of the urban area.  
 319 The emissions of various sources in the urban area were extracted based on their  
 320 spatial distributions. Vehicle POA, VOC (including evaporative emissions), and CO  
 321 emissions in urban area were 1.8, 13.4, and 170.7 k tons, respectively. Vehicles  
 322 dominated CO emission in urban Shanghai, accounting for 85% of total CO emission  
 323 in the urban area.

### 324 **3. Results and discussion**

#### 325 3.1 Vehicle emission inventory

326 The emissions of CO, NO<sub>x</sub>, VOCs, EVA (gas evaporation), EC, and POA  
 327 (OC\*1.2) from vehicles were 343.9, 110.9, 39.4, 8.9, 4.0, and 4.3 k tons in Shanghai  
 328 for the year of 2012 (See Table 3). Gasoline vehicles (including LDGV, Taxi, HDGV,

329 and Motorcycle) were the major sources of CO, VOCs, and EVA emissions,  
330 accounting for 91%, 69%, and 100%, respectively. Diesel vehicles (including LDDV,  
331 HDDV, and Bus) were the major source of NO<sub>x</sub>, EC, and POA emissions, comprising  
332 82%, 99%, and 96%, respectively. CO and VOC (including EVA) emissions  
333 decreased by 40% and 38% compared with the results for the year of 2004 from Wang  
334 et al. (2008). NO<sub>x</sub> emission increased by 21%. PM emission were low estimated in  
335 that article since the PM emission factors were much lower than real-world  
336 measurement data as shown in Fig. 2. Gasoline vehicle emissions have been well  
337 controlled even though their VKTs were nearly doubled in the past few years. In  
338 comparison, the control effect of diesel vehicle emission was relatively poor. It is  
339 clear that diesel exhausts dominate the primary PM (including EC and OA) emissions  
340 in Shanghai. However, since VOC emissions are mainly from gasoline vehicles, we  
341 will further discuss the contributions of gasoline and diesel exhausts to SOA.

### 342 3.2 VOC species of vehicle emissions and gas evaporation

343 Fig. 4 compares the VOC compositions of the exhausts from different vehicle  
344 types and gas evaporation in this study to the results from other countries or regions.  
345 Since the VOC species measured in different studies are not the same, we normalized  
346 the concentrations of the common species including C<sub>2</sub>-C<sub>12</sub> alkanes, alkenes, alkynes,  
347 and single-ring aromatics in each study as 100%. Other compounds and unidentified  
348 VOCs were excluded in the comparison.

349 The weighted percentages of individual VOC for the exhausts from different vehicle  
350 types and gas evaporation were listed in Table S1.

351 The exhausts from gasoline vehicles (including LDGVs and taxis) had similar  
352 VOC compositions. Single-ring aromatics were the major species of the exhausts  
353 from gasoline vehicles, accounting for 50% of the total VOCs approximately.  
354 Straight-chain alkanes, branched alkanes, and cycloalkanes comprised 17.0%, 18.1%,  
355 and 6.1% of the total VOCs, respectively. Toluene, m,p-xylene, o-xylene, and  
356 ethylbenzene were the main compounds in LDGV and taxi exhausts, accounting for

357 7.54%, 6.71%, 5.20%, and 4.42% of the total VOCs, respectively. Motorcycle emitted  
358 more branched alkanes and less single-ring aromatics than LDGVs and taxis.  
359 2-methylhexane (23.43%) was the most abundant VOC in motorcycle exhausts,  
360 followed by m,p-xylene (9.34%), ethylbenzene (5.53%) and o-xylene (4.37%). It was  
361 indicated from Fig. 3 that the proportion of single-ring aromatics in LDGV exhausts  
362 were higher and the proportion of alkene were lower in this and previous studies in  
363 China (Liu et al., 2008; Wang et al., 2013) than those in Hong Kong (Guo et al., 2011)  
364 and US (Schauer et al., 2002; Gentner et al., 2013; May et al., 2014). The differences  
365 of aromatic content in gasoline fuel in different regions and countries could be the  
366 main reason of the difference in the proportion of aromatic compounds in LDGV  
367 exhausts. The limit of aromatic content in current gasoline standard in China was 40  
368 vol%, which was much higher than the limits of gasoline standards of the US (22-25  
369 vol%) and Europe (35 vol%).

370 High proportion of straight-chain alkanes were measured in the exhausts from  
371 diesel vehicles, which accounted for 34.9% and 35.6% of the total VOCs from HDDT  
372 and bus exhausts, respectively. N-dodecane, propene, n-undecane, acetone, and  
373 n-decane were major species in diesel exhausts, accounting for 13.65%, 10.85%,  
374 8.69%, 7.00%, and 6.86% of the total VOCs, respectively. The proportions of  
375 straight-chain alkanes in diesel exhausts in this study were much higher than those in  
376 the previous studies of the US (Schauer et al., 1999; May et al., 2014). Incomplete  
377 combustion of diesel fuel caused by poor engine maintenance could be the main  
378 reason for the high straight-chain alkane emissions.

379 High proportion of alkenes was measured in gas evaporation in this study, which  
380 accounted for 40% of the total VOCs. Propane, isopentane, isobutene, 1-pentene, and  
381 n-butane were major species in gas evaporation emissions, accounting for 15.99%,  
382 11.87%, 9.69%, 8.87%, and 6.51% of the total VOCs, respectively. The proportions of  
383 VOC species in gas evaporation in this study was close to the results in the other  
384 study of China (Zhang et al., 2013), but different from the studies in the US (Harley et

385 al., 2000) and Korea (Na et al., 2004), which reported less alkenes and more branched  
386 alkanes in gas evaporation.

### 387 3.3 SOA yields of different vehicle exhausts and gas evaporation

388 VOC species of vehicle emissions and gas evaporation were classified into 5  
389 categories by their chemical classes, and their distributions of carbon numbers were  
390 shown in Fig. 5(a). Previous studies have confirmed that IVOCs, which were not  
391 detected in this study, played important roles to SOA production (Jathar et al., 2013;  
392 Zhao et al., 2014). For this reason, we combined the amounts of S/IVOCs including  
393 alkanes and aromatic larger than C12 and polycyclic aromatics in unburned fuels  
394 introduced by Gentner et al. (2012). The SOA yields of each vehicle exhaust and  
395 evaporative emission were calculated in two scenarios of with (Y2) or without  
396 S/IVOCs (Y1) in Fig. 5. The carbon numbers of VOCs in gasoline and motorcycle  
397 exhausts mainly concentrated in the intervals between C6 to C9 whether the IVOCs  
398 were merged or not. Comparatively, exhausts from diesel vehicles had a wider  
399 distribution of carbon number, ranging from C2 to C25. More than half of the species  
400 were S/IVOCs and most of them were alkanes. The carbon numbers of VOCs in gas  
401 evaporation were mainly distributed within the range of C3-C7, which were much  
402 smaller than those in vehicle exhausts.

403 Fig. 5(b) and (c) show the SOA mass yields and the contributions of different  
404 chemical class calculate by measured and combined species, respectively. S/IVOC  
405 species had no effect on the SOA yields of gasoline exhausts and evaporative  
406 emissions. Aromatics dominated the yields which accounted for almost 100% of the  
407 total. However, the SOA yield of diesel exhaust was significantly affected by  
408 S/IVOCs. The yield increased from 0.008 to 0.164 when S/IVOCs were considered.  
409 Aromatics were still the largest contributors (34.1%) to but not dominating the yield.  
410 Next were branched alkanes, polycyclic aromatics, and straight-chain alkanes, which  
411 accounted for 24.9%, 17.8%, and 12.8%.

412 The SOA yield of gasoline exhaust was larger than the yield of liquid gasoline

413 reported by Gentner et al. (2012). We found the aromatic contents in gasoline  
414 exhausts of this study which dominated the SOA yield were much higher than those in  
415 the reference. This may be due to the loose limit of aromatics for the gasoline fuel in  
416 China. However, the estimated yield of gasoline exhaust was much lower than the  
417 effective yields (3-30%) of LEV-1 (tier 1 of low emission vehicle standard in  
418 California, US) gasoline vehicles (similar to Euro 1-3 LDGVs tested in this study)  
419 investigated using a smog-chamber experiment by Gordon et al. (2014a). The reason  
420 for the underestimate was still unclear. In contrast, the estimated SOA yield of diesel  
421 exhaust which combined S/IVOCs (Y2) was higher than the average effective yields  
422 ( $9\pm 6\%$ ) for HDDVs without DPF based on smog-chamber experiments by Gordon et  
423 al. (2014b). Since there were few experiments on motorcycle exhaust, we compared  
424 the SOA yield of motorcycle exhaust with the experiment results from the exhausts of  
425 2- and 4-stroke gasoline off-road engines (Gordon et al., 2013). Neither motorcycles  
426 nor off-road engines had catalytic converter. The estimated yield was close to the  
427 experiment results of off-road engine exhausts (2-4%).

428

#### 429 3.4 Primary emission ratio and SOA formation potential based on observation

430 Fig. 7 is a scatterplot of OA versus CO concentrations measured in urban  
431 Shanghai in the summer and the winter of 2013. The observation data were  
432 color-coded by OH exposure ( $\Delta t \cdot [\text{OH}]$ ) determined by equation (4). It was indicated  
433 from the figure that the ratios of OA to CO concentrations generally showed growing  
434 trends with the increase of OH exposure both in summer and winter. The results were  
435 similar to the previous studies in the United States, Japan, and Mexico (Bahreini et al.,  
436 2012; de Gouw et al., 2008; Takegawa et al., 2006; DeCarlo et al., 2008). The primary  
437 emission ratios of POA to CO were determined by the minimum slopes of the  
438 observed OA to CO concentrations, about  $12 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  in both summer and  
439 winter (as shown by the dotted grey lines). The maximum slopes of OA to CO were  
440 50 and  $35 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  (as shown by the dotted black lines) in summer and winter,



441 respectively. The SOA formation ratio in summer was much higher than in winter.  
442 The inventory-based vehicular POA emission to total CO emission was  $11.6$   
443  $\mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  in the urban area of Shanghai (shown by the dotted yellow lines),  
444 almost the same with primary emission ratio observed in the atmosphere, which  
445 indicated that vehicles dominated the POA emissions in urban Shanghai. The dotted  
446 orange line in Fig. 6 represents the maximum OA production ratio (assuming SOA  
447 precursors were 100% reacted) calculated with the SOA yields in Y2 scenario. The  
448 maximum OA production ratio reached  $18.7 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$ . It was considerable  
449 underestimated compared with the observation data, which implied that the SOA  
450 yields derived by known and estimated species were still far from explaining the  
451 actual SOA formation rate in the atmosphere. For this reason, we introduced the  
452 measured SOA yield of gasoline exhaust ( $\sim 0.190$ ) from Gordon et al. (2014a) to  
453 substitute the yield for gasoline vehicles (0,039) in Y2 scenario and defined the new  
454 group as Y3 scenario. The maximum OA production ratio (shown by the dotted red  
455 lines) increased to  $27.3 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$ , but still failed to reach the max. observed  
456  $\Delta\text{OA}/\Delta\text{CO}$ . There must be other emission sources of SOA precursors in the  
457 atmosphere of Shanghai. Previous studies have revealed that VOC emissions from  
458 solvent usage, chemical and petrochemical industrial, and coal burning, etc.  
459 comprised more than 70% of the observed VOCs in the atmosphere of urban Shanghai  
460 (Cai et al., 2010; Wang et al., 2013). The SOA productions of VOC emissions from  
461 these sources also cannot be ignored.

### 462 3.5 Estimation of vehicular OA contribution in the urban atmosphere

463 Fig. 7 shows the diurnal variations of average observed  $\Delta\text{OA}/\Delta\text{CO}$  and OH  
464 exposure in summer and winter. There was a strong correlation between the observed  
465  $\Delta\text{OA}/\Delta\text{CO}$  and OH exposure, which indicated the photooxidation dominated the SOA  
466 formation in the atmosphere. In the role of photochemical reaction, the observed  
467  $\Delta\text{OA}/\Delta\text{CO}$  showed rapid growth trend in the afternoon in summer and reached a peak  
468 around 13:00~14:00. The average observed  $\Delta\text{OA}/\Delta\text{CO}$  in urban atmosphere of

469 Shanghai were  $33.2$  and  $21.1 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  in summer and winter, respectively.

470 To evaluate the contribution of vehicle emission to OA production in urban  
471 atmosphere, we estimated the vehicular OA formation ratio to total CO emissions with  
472 Eq. (5) in two scenarios. Fig. 7(a) and (b) show the results in Y2 scenario. The SOA  
473 yields of gasoline, diesel, and motorcycle exhausts and gas evaporation were 0.039,  
474 0.164, 0.021, and 0.0007, respectively. Fig. 7(c) and (d) show the results in Y3  
475 scenario. The SOA yield of gasoline exhaust was replaced to 0.190 based on the  
476 experiment results (Gordon et al., 2014a). The photochemical age ( $\Delta t$ ) in each hour  
477 was calculated with Eq. (4). Due to the lack of OH measurement in Shanghai, we  
478 referenced the 24-h average OH concentration ( $3\times 10^6$  molecules $\cdot\text{cm}^{-3}$ ) from de Gouw  
479 et al. (2008). The grey and yellow lines were the ratio of vehicular POA and OA  
480 production to total CO emissions. The average vehicular OA production ratios to total  
481 CO emission in the urban area were  $12.5 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  and  $12.2 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  in  
482 summer and winter in Y2 scenario, and  $14.0 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$  and  $13.2 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{ppmv}^{-1}$   
483 in Y3 scenario. The vehicular OA mass accounted for 39% and 58% of the average  
484 observed OA in summer and winter in the urban atmosphere of Shanghai in Y2  
485 scenario. The contributions would increase to 43% and 63% in Y3 scenario. It was  
486 indicated that vehicle emission was the major source of OA mass in the urban  
487 atmosphere of Shanghai. Enhancing the SOA yield of gasoline exhaust increased  
488 about 4%-5% of their contributions to OA, which implied gasoline exhaust didn't  
489 dominate the OA mass in the urban atmosphere. Vehicular SOA formation ratios  
490 accounted for 7%-10% of the total vehicular OA in Y2 scenario and 14%-20% in Y3  
491 scenario. The SOA formation ratios in both scenarios were lower than expected. There  
492 must be other emission sources with high SOA formation potentials in addition to  
493 vehicles in the urban atmosphere. The non-fossil VOC emissions from solvent use,  
494 chemical and petrochemical industrials, etc. reported by the previous studies could be  
495 the rest of contributors (Cai et al., 2010; Wang et al., 2013). Another possible reason  
496 was the SOA yields were still underestimated in this study. There were about 30%,

497 50% and 15% of VOC species still unidentified in gasoline, diesel, and motorcycle  
498 exhausts even after we combined the S/IVOC species reported in Gentner et al. (2012).  
499 The SOA formation potentials of the identified VOC species may contribute more  
500 SOA than expected.

501 At present, few SOA observations in the cities of China can be referenced to  
502 verify the results in this study. Huang et al. (2014) has reported the fossil OA  
503 dominated the OA mass (~40%) in Shanghai based on the observation data in the first  
504 quarter of 2013, which was slightly lower than our result. The possible reason for the  
505 difference could be the location of observation site (close to urban or suburban).  
506 However, the studies both indicated that vehicle emission was the major source of OA  
507 mass in large cities of China.

### 508 3.6 SOA formation contributions of different vehicle types

509 Fig. 9(a) and (b) show the changes of OA formation ratios in different fuel and  
510 vehicle types in Y2 scenario with the increase of the photochemical age. The OA  
511 produced from evaporative emissions were combined in gasoline vehicles and  
512 corresponding vehicle types. Diesel exhausts dominated the OA productions, which  
513 accounted for 96%, 93% and 88% after 0, 6, and 24 hours of photochemical reaction.  
514 HDDV and bus were major sources of OA productions. Fig. 9(c) and (d) show the  
515 changes of OA formation ratios in Y3 scenario. The contribution of gasoline vehicles  
516 in this scenario increased a lot. Although gasoline vehicles only accounted for 4% of  
517 POA emission, their contributions to vehicular OA formation increased to 19% and  
518 35% after 6 and 24 hours of photochemical reaction, respectively. LDGV would be  
519 the second large contributor after HDDV. It can be indicated that diesel vehicles were  
520 the largest contributors to vehicle derived OA in both scenarios although they only  
521 accounted for less than 20% of VKTs in Shanghai. Control of the POA emissions and  
522 SOA precursors from diesel vehicles are equally important. Gasoline vehicle could be  
523 another important contributor to vehicular OA formation. However, there still exist  
524 some debates on the SOA yield of gasoline exhaust. It will be meaningful to find out

525 their actual SOA yield and key precursors for urban OA pollution control.

#### 526 **4. Conclusions**

527 To evaluate the OA contribution of vehicle emissions in the urban atmosphere of  
528 Shanghai, we developed a vehicular emission inventory and estimated the SOA yields  
529 of gasoline, diesel, and motorcycle exhausts and gas evaporation based on measured  
530 C2-C12 VOC species and referenced S/IVOC species from Gentner et al. (2012).  
531 Higher contents of aromatic were measured in this study and other studies in China  
532 compared with the results from the US and European. Loose limit to aromatic  
533 contents in the standard of gasoline fuel in China should be responsible for the high  
534 aromatic contents, which resulted in larger SOA yield of gasoline exhaust than the  
535 results reported by Gentner et al. (2012) based on the same method. However, the  
536 estimated yield was still much lower than the results from smog-chamber experiments  
537 (Gordon et al., 2014a), which implied the unidentified species were considerable to  
538 SOA formation.

539 Vehicles dominated the POA emissions and OA productions in the urban  
540 atmosphere of Shanghai. Their contributions to OA productions were about 40% and  
541 60% in summer and winter, respectively. The rest of the contributors could be the  
542 non-fossil VOC emissions from solvent use, chemical and petrochemical industrials,  
543 etc. and the underestimated SOA productions from unidentified VOC or IVOC  
544 species in the exhausts. At present, vehicles are experiencing rapid growth trends in  
545 the cities of China. Primary emissions and secondary formation of OA derived from  
546 vehicles will lead to further deterioration of fine particle pollution in the urban area.  
547 Reduction of primary PM emissions and SOA precursors from vehicle exhausts will  
548 be helpful to improve the air quality in the cities of China. The results also indicate  
549 diesel exhausts dominate the POA emissions in the urban area. Therefore,  
550 strengthening the primary PM emission control of diesel vehicles, especially for the  
551 older diesel vehicles with loose emission standards as shown by Fig. 2, plays an  
552 important role in OA pollution prevention. Now China is conducting the large-scale

553 elimination of “yellow-labeled” diesel vehicles whose emission standards were lower  
554 than Euro 3. It can be expected to effectively reduce the OA pollution caused by  
555 diesel vehicles. On the other hand, gasoline exhausts have high potential impacts on  
556 SOA formation in the urban area. Tightening the limit of aromatic contents in gasoline  
557 fuel will be meaningful to reduce the SOA contributions of gasoline vehicles.

558 There are still some uncertainties need to be improved in the future. First is the  
559 SOA mass yield. More experiments on SOA yields of vehicle exhausts in China will  
560 be helpful to the SOA formation potentials of different vehicle types. Especially for  
561 gasoline exhausts, the estimated SOA yield was much lower than the experiment  
562 results in the US. Vehicular OA contributions will increase about 4%-5% if we replace  
563 the estimated SOA yield of gasoline exhaust to the experiment result. It will be  
564 meaningful to find out their actual SOA yield and key precursors for urban OA  
565 pollution control. Emission inventory is another important source of uncertainty in  
566 this study. To reduce the uncertainty of vehicular emission inventory, we localized the  
567 vehicle mileage and emission factor data based on the traffic surveys in Shanghai and  
568 real-world measurements in some cities of China. However, the CO emission  
569 inventories of other sources shown in Fig. S5 still have large uncertainties according  
570 to the previous study (Huang et al., 2011). More accurate emission inventory will be  
571 helpful to reduce the uncertainty of vehicular OA contribution in this study. However,  
572 it can be concluded that vehicle emissions are the most important contributors to OA  
573 pollution in the cities of China. Another implication is the potential roles of IVOCs in  
574 vehicle exhausts are very important on the SOA formation in the urban area.  
575 Therefore, further studies need to pay more attentions to determine the contributions  
576 of IVOC emissions to OA pollution in China.

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### 583 **References**

- 584 Bahreini, R., Middlebrook, A. M., de Gouw, J. A., Warneke, C., Trainer, M., Brock, C. A.,  
585 Stark, H., Brown, S. S., Dube, W. P., Gilman, J. B., Hall, K., Holloway, J. S., Kuster, W.  
586 C., Perring, A. E., Prévôt, A. S. H., Schwarz, J. P., Spackman, J. R., Szidat, S., Wagner, N.  
587 L., Weber, R. J., Zotter, P., and Parrish, D. D.: Gasoline emissions dominate over diesel  
588 in formation of secondary organic aerosol mass, *Geophys. Res. Lett.*, 39, L06805,  
589 doi:10.1029/2011GL050718, 2012.
- 590 Borbon, A., Gilman, J. B., Kuster, W. C., Grand, N., Chevallier, S., Colomb, A., Dolgorouky,  
591 C., Gros, V., Lopez, M., Sarda-Esteve, R., Holloway, J., Stutz, J., Petetin, H., McKeen, S.,  
592 Beekmann, M., Warneke, C., Parrish, D. D., and de Gouw, J. A.: Emission ratios of  
593 anthropogenic volatile organic compounds in northern mid-latitude megacities:  
594 Observations versus emission inventories in Los Angeles and Paris, *J. Geophys.*  
595 *Res.-Atmos.*, 118, 2041–2057, doi:10.1002/jgrd.50059, 2013
- 596 Cai, C. J., Geng, F. H., Tie, X. X., Yu, Q., An, J. L.: Characteristics and source apportionment  
597 of VOCs measured in Shanghai, China, *Atmospheric Environment*, 44, 5005–5014,  
598 2010.
- 599 Cao, J. J., Zhu, C. S., Tie, X. X., Geng, F. H., Xu, H. M., Ho, S. S. H., Wang, G. H., Han, Y.  
600 M., Ho, K.F.: Characteristics and sources of carbonaceous aerosols from Shanghai,  
601 China. *Atmos. Chem. Phys.*, 13, 803–817, 2013.
- 602 Chan, A. W. H., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crouse, J. D.,  
603 Kürten, A., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic  
604 aerosol formation from photooxidation of naphthalene and alkylnaphthalenes:  
605 implications for oxidation of intermediate volatility organic compounds (IVOCs), *Atmos.*  
606 *Chem. Phys.*, 9, 3049–3060, doi:10.5194/acp-9-3049-2009, 2009.
- 607 Chen, C. H., Huang, C., Jing, Q. G., Wang, H. K., Pan, H. S., Li, L., Zhao, J., Dai, Y., Huang,  
608 H. Y., Schipper, L., Streets, D. G.: On-road emission characteristics of heavy-duty diesel

609 vehicles in Shanghai, *Atmospheric Environment*, 41, 5334-5344, 2007.

610 Chirico, R., DeCarlo, P. F., Heringa, M. F., Tritscher, T., Richter, R., Prévôt, A. S. H.,  
611 Dommen, J., Weingartner, E., Wehrle, G., Gysel, M., Laborde, M., and Baltensperger, U.:  
612 Impact of aftertreatment devices on primary emissions and secondary organic aerosol  
613 formation potential from in-use diesel vehicles: results from smog chamber experiments,  
614 *Atmos. Chem. Phys.*, 10, 11545–11563, doi:10.5194/acp-10-11545-2010, 2010.

615 DeCarlo, P. F., Dunlea, E. J., Kimme, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P.  
616 O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R.,  
617 Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., Jimenez, J. L.: Fast airborne  
618 aerosol size and chemistry measurements above Mexico City and Central Mexico during  
619 the MILAGRO campaign, *Atmos. Chem. Phys.*, 8, 4027–4048, 2008.

620 de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M.,  
621 Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C.,  
622 Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted  
623 atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys.*  
624 *Res.-Atmos.*, 110, D16305, doi:10.1029/2004jd005623, 2005.

625 de Gouw, J. A., Brock, C. A., Atlas, E. L., Bates, T. S., Fehsenfeld, F. C., Goldan, P. D.,  
626 Holloway, J. S., Kuster, W. C., Lerner, B. M., Matthew, B. M., Middlebrook, A. M.,  
627 Onasch, T. B., Peltier, R. E., Quinn, P. K., Senff, C. J., Stohl, A., Sullivan, A. P., Trainer,  
628 M., Warneke, C., Weber, R. J., and Williams, E. J.: Sources of particulate matter in the  
629 northeastern United States in summer: 1. Direct emissions and secondary formation of  
630 organic matter in urban plumes, *J. Geophys. Res.-Atmos.*, 113, D08301,  
631 doi:08310.01029/02007JD009243, 2008.

632 de Gouw, J. and Jimenez, J. L.: Organic Aerosols in the Earth's Atmosphere, *Environ. Sci.*  
633 *Technol.*, 43, 7614–7618, 2009.

634 Feng, J. L., Chan, C. K., Fang, M., Hu, M., He, L. Y., Tang, X. Y.: Characteristics of organic  
635 matter in PM<sub>2.5</sub> in Shanghai, *Chemosphere*, 64, 1393-1400, 2005.

636 Feng, J. L., Li, M., Zhang, P., Gong, S. Y., Zhong, M., Wu, M. H., Zheng, M., Chen, C. H.,

637 Wang, H. L., Lou, S. R.: Investigation of the sources and seasonal variations of  
638 secondary organic aerosols in PM<sub>2.5</sub> in Shanghai with organic tracers, *Atmospheric*  
639 *Environment*, 79, 614-622, 2013.

640 Feng, Y. L., Chen, Y. J., Guo, H., Zhi, G. R., Xiong, S. C., Li, J., Sheng, G. Y., Fu, J. M.:  
641 Characteristics of organic and elemental carbon in PM<sub>2.5</sub> samples in Shanghai, China,  
642 *Atmospheric Research*, 92, 434-442, 2009.

643 Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu,  
644 S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Uha, A., Harley, R. A., and  
645 Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline  
646 vehicles through detailed characterization of organic carbon emissions, *P. Natl. Acad. Sci.*  
647 *USA*, 109, 18318–18323, 2012.

648 Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L. C., Dallmann, T. R., Wood, E. C.,  
649 Herndon, S. C., Goldstein, A. H., Harley, R. A.: Chemical composition of gas-phase  
650 organic carbon emissions from motor vehicles and implications for ozone production,  
651 *Environ. Sci. Technol.*, 47, 11837–11848, 2013.

652 Gordon, T. D., Tkacik, D. S., Presto, A. A., Zhang, M., Jathar, S. H., Nguyen, N. T., Massetti,  
653 J., Truong, T., Cicero-Fernandez, P., Maddox, C., Rieger, P., Chattopadhyay, S.,  
654 Maldonado, H., Maricq, M. M., Robinson, A. L.: Primary gas- and particle-phase  
655 emissions and secondary organic aerosol production from gasoline and diesel off-road  
656 engines, *Environ. Sci. Technol.*, 47, 14137–14146, 2013.

657 Gordon, T. D., Presto, A. A., May, A. A., Nguyen, N. T., Lipsky, E. M., Donahue, N. M.,  
658 Gutierrez, A., Zhang, M., Maddox, C., Rieger, P., Chattopadhyay, S., Maldonado, H.,  
659 Maricq, M. M., Robinson, A. L.: Secondary organic aerosol formation exceeds primary  
660 particulate matter emissions for light-duty gasoline vehicles, *Atmos. Chem. Phys.*, 14,  
661 4661–4678, 2014a.

662 Gordon, T. D., Presto, A. A., Nguyen, N. T., Robertson, W. H., Na, K., Sahay, K. N., Zhang,  
663 M., Maddox, C., Chattopadhyay, S., Maldonado, H., Maricq, M. M., Robinson, A. L.:  
664 Secondary organic aerosol production from diesel vehicle exhaust: impact of



665        aftertreatment, fuel chemistry and driving cycle, *Atmos. Chem. Phys.*, 14, 4643–4659,  
666        2014b.

667    Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of  
668        photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass  
669        spectrometer data, *Atmos. Chem. Phys.*, 9, 2227–2240, 2009.

670    Guo, H., Zou, S. C., Tsai, W. Y., Chan, L. Y., Blake, D. R.: Emission characteristics of  
671        nonmethane hydrocarbons from private cars and taxis at different driving speeds in Hong  
672        Kong, *Atmospheric Environment*, 45, 2711–2721, 2011.

673    Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M.,  
674        Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann,  
675        H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A.,  
676        Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J.  
677        H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of  
678        secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9,  
679        5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

680    Harley, R. A., Coulter-Burke, S. C., Yeung, T. S.: Relating liquid fuel and headspace vapor  
681        composition for California reformulated gasoline samples containing ethanol, *Environ.*  
682        *Sci. Technol.*, 34, 4088–4094, 2000.

683    Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W.,  
684        Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappengluck, B.,  
685        Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., de Gouw, J. A.,  
686        Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corrigan, A. L., Russell, L. M., Isaacman, G.,  
687        Worton, D. R., Kreisberg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M.,  
688        Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Offenberg, J. H., Dusanter, S.,  
689        Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., Jimenez, J. L.: Organic aerosol  
690        composition and sources in Pasadena, California during the 2010 CalNex Campaign, *J.*  
691        *Geophys. Res.-Atmos.*, 118, 9233–9257, doi:10.1002/jgrd.50530, 2013.

692    Hou, B., Zhuang, G. S., Zhang, R., Liu, T. N., Guo, Z. G., Chen, Y.: The implication of

693 carbonaceous aerosol to the formation of haze: Revealed from the characteristics and  
694 sources of OC/EC over a mega-city in China, *Journal of Hazardous Materials*, 190,  
695 529–536, 2011.

696 Huang, C., Chen, C. H., Li, L., Cheng, Z., Wang, H. L., Huang, H. Y., Streets, D. G., Wang, Y.  
697 J., Zhang, G. F., and Chen, Y. R.: Emission inventory of anthropogenic air pollutants and  
698 VOC species in the Yangtze River Delta region, China, *Atmos. Chem. Phys.*, 11,  
699 4105–4120, doi:10.5194/acp-11-4105-2011, 2011.

700 Huang, C., Lou, D. M., Hu, Z. Y., Feng, Q., Chen, Y. R., Chen, C. H., Tan, P. Q., Yao, D.: A  
701 PEMS study of the emissions of gaseous pollutants and ultrafine particles from gasoline-  
702 and diesel-fueled vehicles, *Atmospheric Environment*, 77, 703–710, 2013.

703 Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R.,  
704 Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A.,  
705 Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G.,  
706 Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I.,  
707 Prévôt, A. S. H.: High secondary aerosol contribution to particulate pollution during haze  
708 events in China, *Nature*, 514, 218–222, doi:10.1038/nature13774, 2014.

709 Huang, X. F., He, L. Y., Xue, L., Sun, T. L., Zeng, L. W., Gong, Z. H., Hu, M., Zhu, T.: Highly  
710 time-resolved chemical characterization of atmospheric fine particles during 2010  
711 Shanghai World Expo, *Atmos. Chem. Phys.*, 12, 4897–4907,  
712 doi:10.5194/acp-12-4897-2012, 2012.

713 Huang, X. F., Xue, L., Tian, X. D., Shao, W. W., Sun, T. L., Gong, Z. H., Ju, W. W., Jiang, B.,  
714 Hu, M., He, L. Y.: Highly time-resolved carbonaceous aerosol characterization in  
715 Yangtze River Delta of China: Composition, mixing state and secondary formation,  
716 *Atmospheric Environment*, 64, 200–207, 2013.

717 Hung, H. F. and Wang, C. S.: Formation of secondary organic aerosols and reactive oxygen  
718 species from diluted motorcycle exhaust, *J. Chin. Inst. Chem. Eng.*, 37, 491–499, 2006.

719 Huo, H., Yao, Z. L., Zhang, Y. Z., Shen, X. B., Zhang, Q., Ding, Y., He, K. B.: On-board  
720 measurements of emissions from light-duty gasoline vehicles in three mega-cities of

721 China, *Atmospheric Environment*, 49, 371-377, 2012a.

722 Huo, H., Yao, Z. L., Zhang, Y. Z., Shen, X. B., Zhang, Q., He, K. B.: On-board measurements  
723 of emissions from diesel trucks in five cities in China, *Atmospheric Environment*, 54,  
724 159-167, 2012b.

725 Jathar, S. H., Miracolo, M. A., Tkacik, D. S., Donahue, N. M., Adams, P. J., and Robinson, A.  
726 L.: Secondary organic aerosol formation from photo-oxidation of unburned fuel:  
727 Experimental results and implications for aerosol formation from combustion emissions,  
728 *Environ. Sci. Technol.*, 47, 12886–12893, 2013.

729 Jimenez, J. L.: Ph. D thesis of Understanding and quantifying motor vehicle emissions with  
730 vehicle specific power and TILDAS remote sensing, Massachusetts: Massachusetts  
731 Institute of Technology, 1999.

732 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prévôt, A. S. H., Zhang, Q., et al.:  
733 Evolution of organic aerosols in the atmosphere, *Science*, 326 (5959), 1525–1529, 2009.

734 Kleindienst, T. E., Corse, E.W., Li,W., McIver, C. D., Conner, T. S., Edney, E. O., Driscoll, D.  
735 J., Speer, R. E., Weathers, W. S., and Tejada, S. B.: Secondary organic aerosol formation  
736 from the irradiation of simulated automobile exhaust, *J Air Waste Manage.*, 52, 259–272,  
737 2002.

738 Liu, S., Ahlm, L., Day, D. A., Russell, L. M., Zhao, Y. L., Gentner, D. R., Weber, R. J.,  
739 Goldstein, A. H., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Rubitschun, C., Surratt,  
740 J. D., Sheesley, R. J., and Scheller, S.: Secondary organic aerosol formation from fossil  
741 fuel sources contribute majority of summertime organic mass at Bakersfield, *J. Geophys.*  
742 *Res.-Atmos.*, 117, D00V26, doi:10.1029/2012JD018170, 2012

743 Liu, Y., Shao, M., Fu, L. L., Lu, S.H., Zeng, L. M., Tang, D. G.: Source profiles of volatile  
744 organic compounds (VOCs) measured in China: Part I, *Atmospheric Environment*, 42,  
745 6247–6260, 2008.

746 May, A.A., Nguyen, N.T., Presto, A.A., Gordon, T.D., Lipsky, E.M., Karve, M., Gutierrez, A.,  
747 Robertson, W.H., Zhang, M., Brandow, C., Chang, O., Chen, S., Cicero-Fernandez, P.,  
748 Dinkins, L., Fuentes, M., Huang, S.M., Ling, R., Long, J., Maddox, C., Massetti, J.,

749 McCauley, E., Miguel, A., Na, K., Ong, R., Pang, Y., Rieger, P., Sax, T., Truong, T., Vo,  
750 T., Chattopadhyay, S., Maldonado, H., Maricq, M.M., Robinson, A.L.: Gas- and  
751 particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles,  
752 *Atmospheric Environment*, 88, 247–260, 2014.

753 Na, K., Kim, Y. P., Moon, I., Moon, K. C.: Chemical composition of major VOC emission  
754 sources in the Seoul atmosphere, *Chemosphere*, 55, 585–594, 2004.

755 Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.:  
756 Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos.*  
757 *Chem. Phys.*, 7, 3909–3922, doi:10.5194/acp-7-3909-2007, 2007.

758 Nordin, E. Z., Eriksson, A. C., Roldin, P., Nilsson, P. T., Carlsson, J. E., Kajos, M. K., Hellén,  
759 H., Wittbom, C., Rissler, J., Löndahl, J., Swietlicki, E., Svenningsson, B., Bohgard, M.,  
760 Kulmala, M., Hallquist, M., and Pagels, J. H.: Secondary organic aerosol formation from  
761 idling gasoline passenger vehicle emissions investigated in a smog chamber, *Atmos.*  
762 *Chem. Phys.*, 13, 6101–6116, doi:10.5194/acp-13-6101-2013, 2013.

763 Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld,  
764 J. H.: Aromatics, reformulated gasoline, and atmospheric organic aerosol formation,  
765 *Environ. Sci. Technol.*, 31, 1890–1897, 1997.

766 Platt S. M., El Haddad, I., Zardini, A. A., Clairotte, M., Astorga, C., Wolf, R., Slowik, J. G.,  
767 Temime-Roussel, B., Marchand, N., Ježek, I., Drinovec, L., Močnik, G., Möhler, O.,  
768 Richter, R., Barmet, P., Bianchi, F., Baltensperger, U., and Prévôt, A. S. H.: Secondary  
769 organic aerosol formation from gasoline vehicle emissions in a new mobile  
770 environmental reaction chamber, *Atmos. Chem. Phys.*, 13, 9141–9158,  
771 doi:10.5194/acp-13-9141-2013, 2013.

772 Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M.,  
773 Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols:  
774 Semivolatile emissions and photochemical aging, *Science*, 315, 1259–1262, 2007.

775 SCCTPI (Shanghai City Comprehensive Transportation Planning Institute): Shanghai  
776 comprehensive transportation annual report, Shanghai, 2012.

777 Schauer, J. J., Kleeman, M., Cass, G., Simoneit, B. T.: Measurement of emissions from air  
778 pollution sources. 2. C1 through C30 organic compounds from medium duty diesel  
779 trucks, *Environ. Sci. Technol.*, 33, 1578–1587, 1999.

780 Schauer, J. J., Kleeman, M., Cass, G., Simoneit, B. T.: Measurement of emissions from air  
781 pollution sources. 5. C1-C32 organic compounds from gasoline-powered motor vehicles,  
782 *Environ. Sci. Technol.*, 36, 1169–1180, 2002.

783 Stone, E. A., Zhou, J., Snyder, D. C., Rutter, A. P., Mieritz, M., and Schauer, J. J.: A  
784 comparison of summertime secondary organic aerosol source contributions at contrasting  
785 urban locations, *Environ. Sci. Technol.*, 43, 3448–3454, 2009.

786 Takegawa, N., Miyakawa, T., Kondo, Y., Jimenez, J. L., Zhang, Q., Worsnop, D. R., Fukuda,  
787 M.: Seasonal and diurnal variations of submicron organic aerosol in Tokyo observed  
788 using the Aerodyne aerosol mass spectrometer, *J. Geophys. Res.-Atmos.*, 111, D11206,  
789 doi:10.1029/2005JD006515, 2006.

790 Turpin, B. J. and Lim, H. J.: Species contributions to PM<sub>2.5</sub> mass concentrations: Revisiting  
791 common assumptions for estimating organic mass, *Aerosol Science and Technology*, 35,  
792 602-610, 2001.

793 Wang, H. K., Chen, C. H., Huang, C., Fu, L.X.: On-road vehicle emission inventory and its  
794 uncertainty analysis for Shanghai, China. *Science of the Total Environment*, 398, 60–67,  
795 2008.

796 Wang, H. L., Chen, C. H., Wang, Q., Huang, C., Su, L. Y., Huang, H. Y., Lou, S. R., Zhou, M.,  
797 Li, L., Qiao, L. P., Wang, Y. H.: Chemical loss of volatile organic compounds and its  
798 impact on the source analysis through a two-year continuous measurement, *Atmospheric*  
799 *Environment*, 80, 488–498, 2013.

800 Wang, J., Jin, L. M., Gao, J. H., Shi, J. W., Zhao, Y. L., Liu, S. X., Jin, T. S., Bai, Z. P., Wu, C.  
801 Y.: Investigation of speciated VOC in gasoline vehicular exhaust under ECE and  
802 EUDC test cycles, *Science of the Total Environment*, 445–446, 110–116, 2013.

803 Warneke, C., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Williams, E. J., Lerner, B. M.,  
804 Jakoubek, R., Brown, S. S., Stark, H., Aldener, M., Ravishankara, A. R., Roberts, J. M.,

805 Marchewka, M., Bertman, S., Sueper, D. T., McKeen, S. A., Meagher, J. F., and  
806 Fehsenfeld, F. C.: Comparison of daytime and nighttime oxidation of biogenic and  
807 anthropogenic VOCs along the New England coast in summer during New England Air  
808 Quality Study 2002, *J. Geophys. Res.-Atmos.*, 109, D10309, doi:10.1029/2003jd004424,  
809 2004.

810 Weitkamp, E. A., Sage, A. M., Pierce, J. R., Donahue, N. M., and Robinson, A. L.: Organic  
811 aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber,  
812 *Environ. Sci. Technol.*, 41, 6969–6975, 2007.

813 Wu, Y., Zhang, S. J., Li, M. L., Ge, Y. S., Shu, J. W., Zhou, Y., Xu, Y. Y., Hu, J. N., Liu, H., Fu,  
814 L. X., He, K. B., Hao, J. M.: The challenge to NO<sub>x</sub> emission control for heavy-duty  
815 diesel vehicles in China, *Atmos. Chem. Phys.*, 12, 9365–9379, 2012.

816 Ye, B. M., Ji, X. L., Yang, H. Z., Yao, X. H., Chan, C. K., Cadle, S. H., Chan, T., Mulawa, P.  
817 A.: Concentration and chemical composition of PM<sub>2.5</sub> in Shanghai for a 1-year period,  
818 *Atmospheric Environment*, 37, 499–510, 2003.

819 Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.:  
820 VOC emissions, evolutions and contributions to SOA formation at a receptor site in  
821 eastern China, *Atmos. Chem. Phys.*, 13, 8815–8832, doi:10.5194/acp-13-8815-2013,  
822 2013.

823 Zhang, Y. L., Wang, X. M., Zhang, Z., Lü, S. J., Shao, M., Lee, S. C., Yu, J. Z.: Species  
824 profiles and normalized reactivity of volatile organic compounds from gasoline  
825 evaporation in China, *Atmospheric Environment*, 79, 110–118, 2013.

826 Zhao, Y. L., Hennigan, C. J., May, A. A., Tkacik, D. S., de Gouw, J. A., Gilman, J. B., Kuster,  
827 W. C., Borbon, A., Robinson, A. L.: Intermediate-volatility organic compounds: a large  
828 source of secondary organic aerosol, *Environ. Sci. Technol.*, 48, 13743–13750, 2014.

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830 **Table 1.** Daily VKT and average speeds of various vehicle and road types in Shanghai in 2012.

Road types	Daily vehicle kilometers traveled (million km)							Total	Average speed (km·h <sup>-1</sup> )
	Light-duty car	Light-duty truck	Taxi	Heavy-duty bus	Heavy-duty truck	City bus	Motor-cycle		
Highway	38.3	0.62	3.96	3.10	11.82	0.23	0.00	58.04	57.9
Arterial road	22.6	2.93	6.16	1.12	4.73	1.58	5.29	44.41	36.0
Residential road	18.3	3.11	8.92	0.89	1.90	1.38	4.15	38.64	28.5
Total	79.2	6.66	19.04	5.11	18.45	3.19	9.44	141.09	43.0

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833 **Table 2.** Test vehicle specifications.

ID	Vehicle type	Fuel type	Emission standard	Model year	Odometer reading (km)
LDGV-1	Light-duty car	Gasoline	Euro 1	2002	245306
LDGV-2	Light-duty car	Gasoline	Euro 2	2005	59790
LDGV-3	Light-duty car	Gasoline	Euro 3	2008	87662
LDGV-4	Light-duty car	Gasoline	Euro 3	2008	80856
Taxi-1	Light-duty taxi	Gasoline	Euro 1	2001	270000
Taxi-2	Light-duty taxi	Gasoline	Euro 1	2002	~100000
Taxi-3	Light-duty taxi	Gasoline	Euro 2	2003	99638
Taxi-4	Light-duty taxi	Gasoline	Euro 3	2007	281315
Taxi-5	Light-duty taxi	Gasoline	Euro 3	2008	361180
HDDT-1	Heavy-duty truck	Diesel	Euro 1	2003	331387
HDDT-2	Heavy-duty truck	Diesel	Euro 1	2003	271000
HDDT-3	Heavy-duty truck	Diesel	Euro 2	2004	271125
HDDT-4	Heavy-duty truck	Diesel	Euro 2	2004	204193
HDDT-5	Heavy-duty truck	Diesel	Euro 3	2009	70000
Bus-1	City bus	Diesel	Euro 2	2006	295236
Bus-2	City bus	Diesel	Euro 3	2006	175122
MT-1	Motorcycle	Gasoline	Euro 1	2003	15000
MT-2	Motorcycle	Gasoline	Euro 1	2003	11191
MT-3	Motorcycle	Gasoline	Euro 2	2004	96969
MT-4	Motorcycle	Gasoline	Euro 2	2003	13912
MT-5	Motorcycle	Gasoline	Euro 2	2003	5379

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**Table 3.** Vehicle emission inventory in Shanghai.

Vehicle type	Emission inventory (k ton)					POA (OC*1.2)
	CO	NOx	VOCs	EVA	EC	
in vehicle type						
LDGV	192.03	13.30	15.59	6.15	0.02	0.07
LDDV	1.89	5.72	0.32	0.00	0.17	0.11
Taxi	68.89	3.86	5.56	1.96	0.01	0.03
HDGV	36.79	2.20	2.29	0.29	0.00	0.01
HDDV	24.71	67.56	9.74	0.00	3.16	3.40
Bus	5.53	17.56	2.06	0.00	0.58	0.62
Motorcycle	14.01	0.67	3.85	0.49	0.02	0.06
in fuel type						
Gasoline	311.71	20.04	27.28	8.88	0.05	0.17
Diesel	32.14	90.84	12.12	0.00	3.91	4.13
Total	343.85	110.88	39.40	8.88	3.96	4.30

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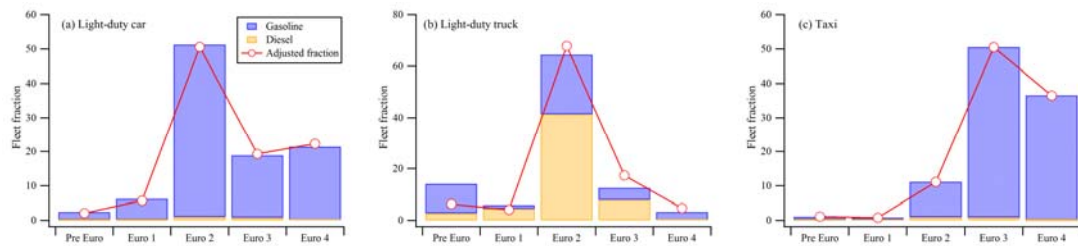
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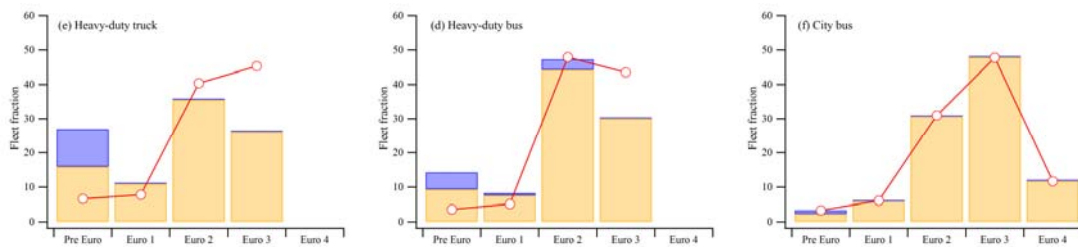
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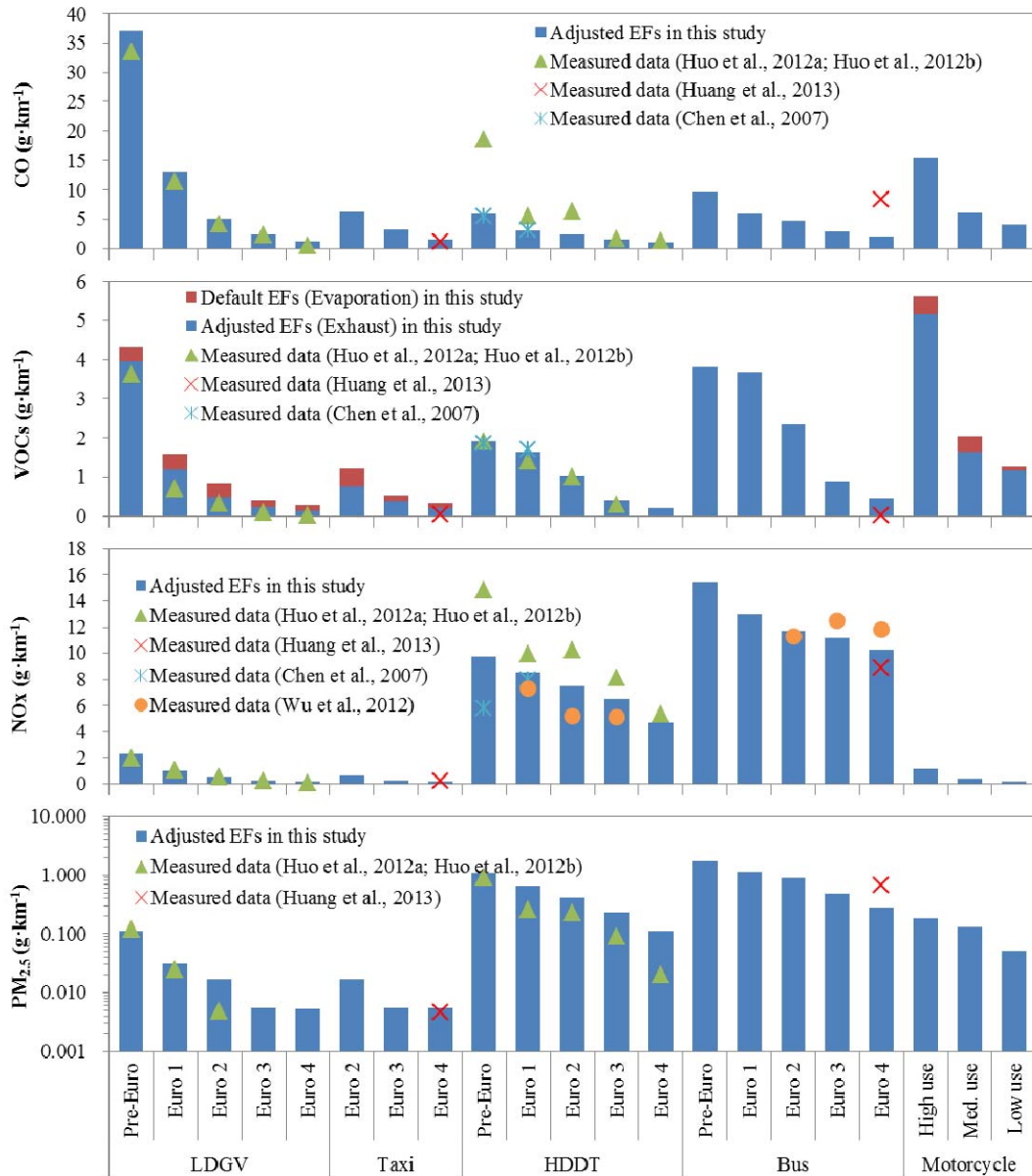
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**Fig. 1.** Static and adjusted fractions of each vehicle type in Shanghai.

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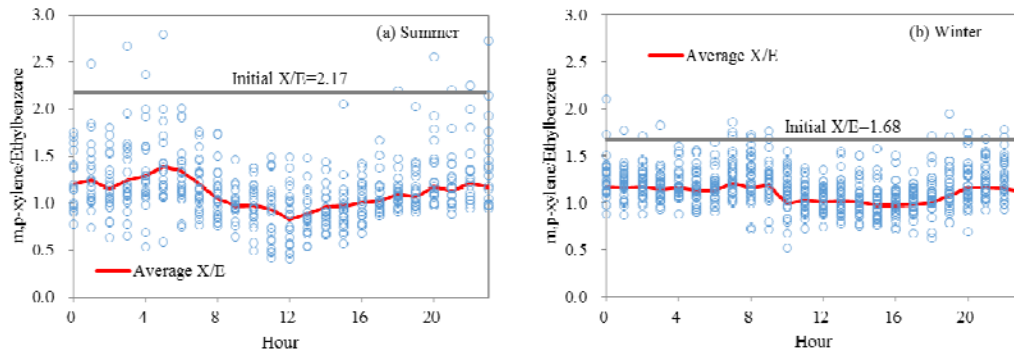
854 **Fig. 2.** Adjusted emission factors of various vehicle types (blue bars) and their comparisons with

855 measured emission factors in the previous studies (dots).

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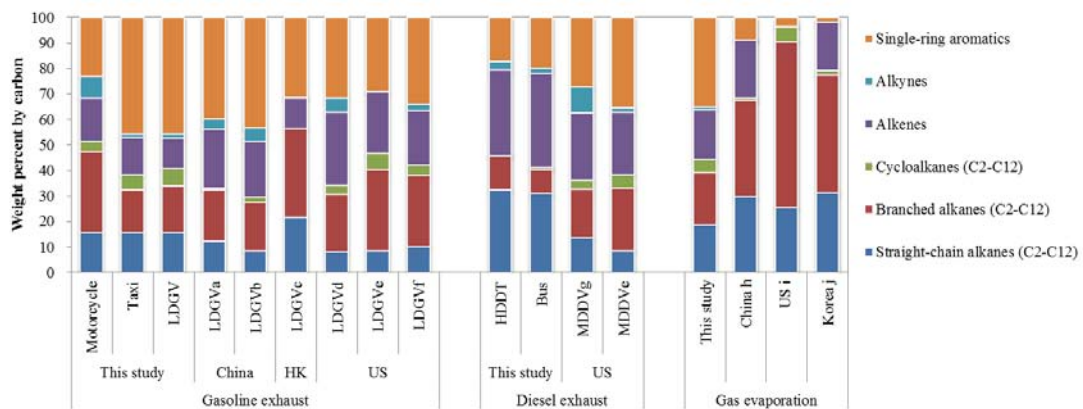
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860 **Fig. 3.** Diurnal distributions of the ratios of m,p-xylene to ethylbenzene concentrations in summer  
 861 and winter in the urban atmosphere in 2013.

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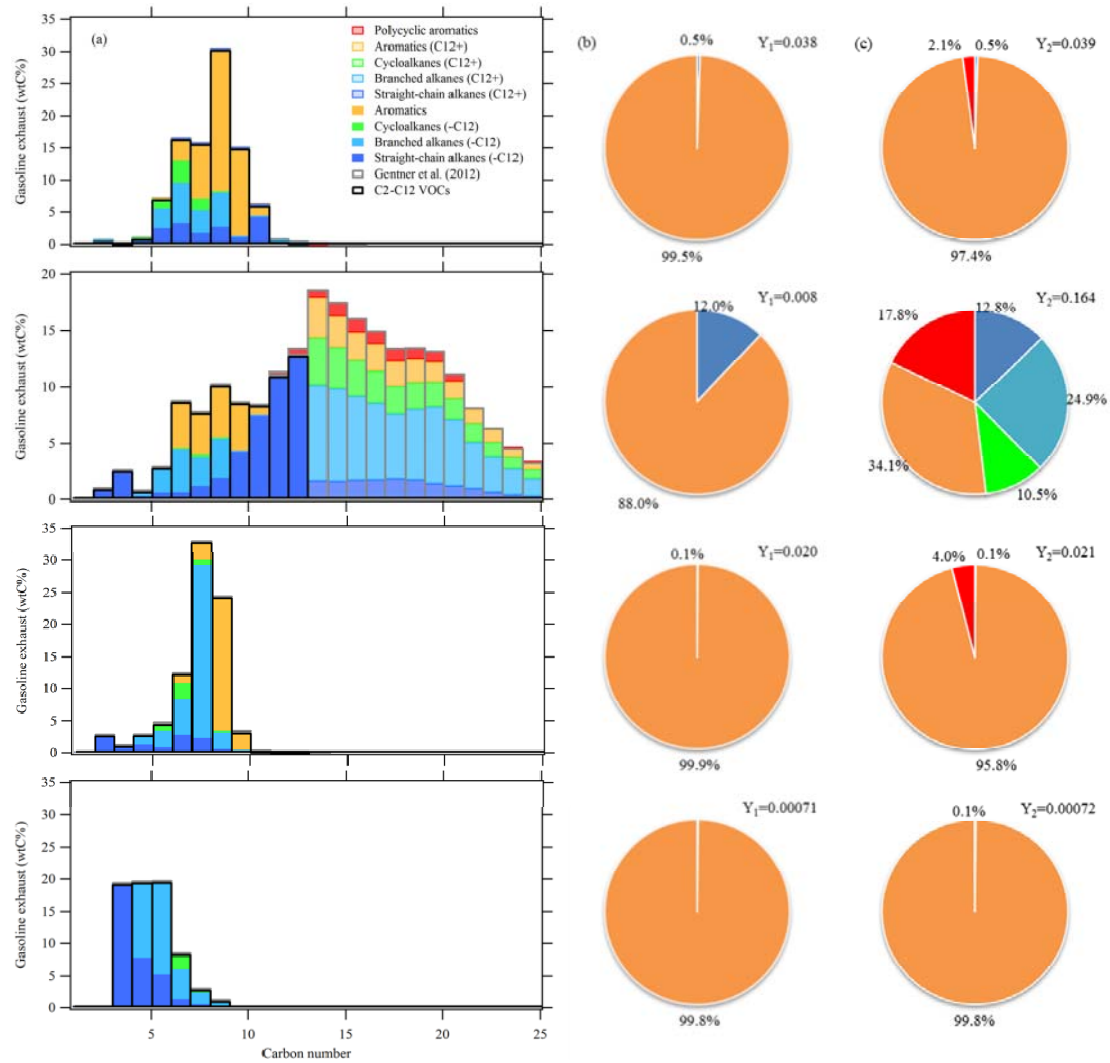
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866 **Fig. 4.** Comparisons of measured VOC compositions of the exhausts from different vehicle types  
 867 and gas evaporation to the results in other studies (a. Liu et al., 2008; b. Wang et al., 2013; c. Guo  
 868 et al., 2011; d. Schauer et al., 2002; e. May et al., 2014; f. Gentner et al., 2013; g. Schauer et al.,  
 869 1999; h. Zhang et al., 2013; i. Harley et al., 2000; j. Na et al., 2004).

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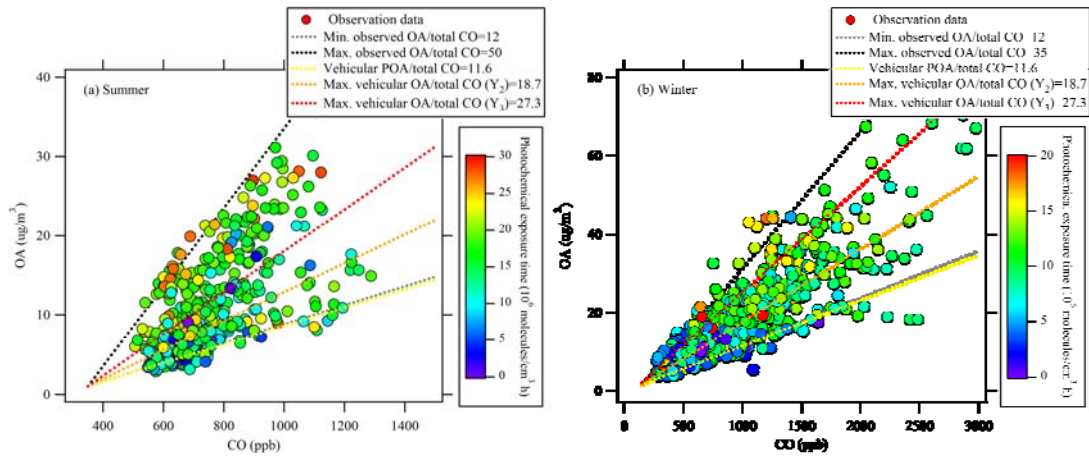
874 **Fig. 5.** (a) Distribution of mass by chemical class in carbon number of different vehicle exhausts  
 875 and evaporative emissions; (b) Calculated SOA yields based on C2-C12 VOCs measured in this  
 876 study and their contributors; (c) Calculated SOA yields based on C2-C25 VOCs combined with  
 877 S/IVOC species in unburned fuel referenced from Gentner et al. (2012) and their contributors.

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883 **Fig. 6.** Relationship of measured OA and CO concentrations color-coded by the photochemical

884 exposure in the summer (a) and winter (b) of 2013 in urban Shanghai according to equation (4).

885 Minimum and maximum ratios of observed OA to CO concentrations are shown by dotted grey

886 and black lines. Vehicular POA/Total CO is shown by dotted yellow line. The minimum and

887 maximum OA formation ratios of vehicle emissions calculated with two different SOA yields of

888  $Y_2$  and  $Y_3$  are shown by the dotted orange and red lines, respectively.

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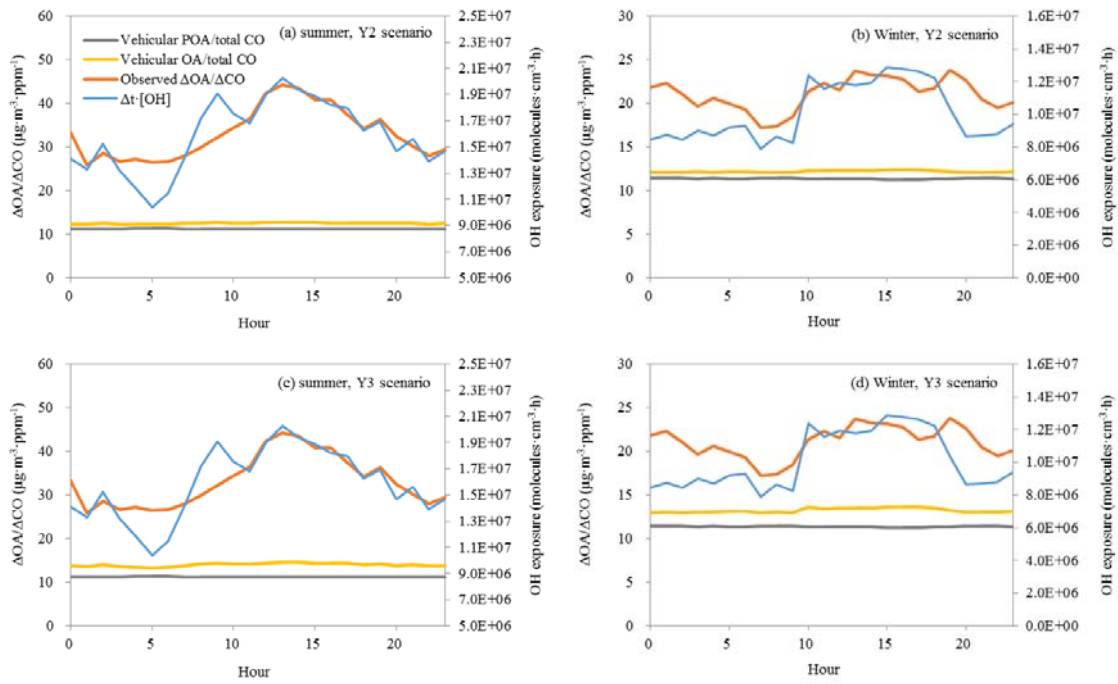
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901 **Fig. 7.** Diurnal variations of observed  $\Delta\text{OA}/\Delta\text{CO}$  in the atmosphere (red line), OH exposures (blue  
 902 line), and the ratios of vehicular POA emission (grey line) and OA formation (orange line) to total  
 903 CO emissions with the SOA yields in two scenarios (Y2 and Y3) in summer and winter in the  
 904 urban area of Shanghai for the year of 2013.

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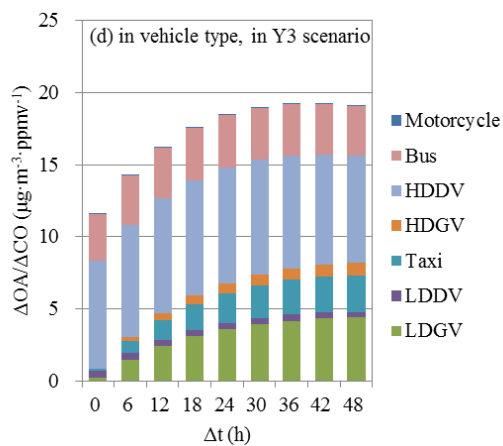
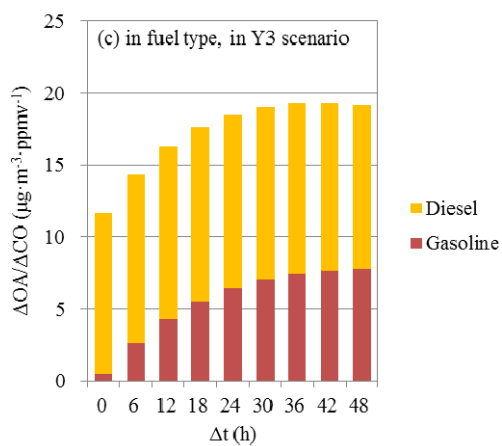
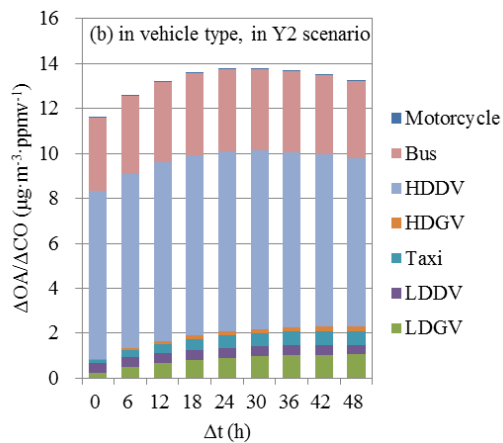
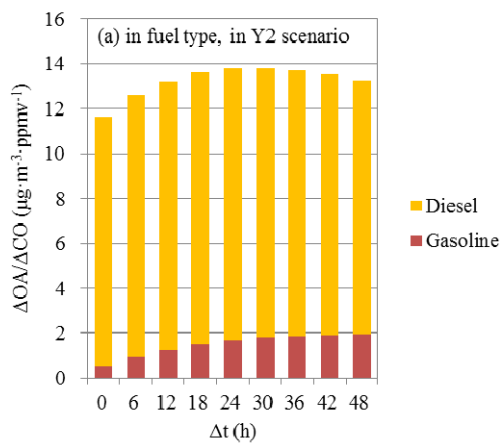
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918 **Fig. 8.** Contributions of vehicle emissions to OA formation ratios in different vehicle and fuel  
 919 types in Y2 and Y3 scenarios with the changes of photochemical ages.

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