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DOI:

[10.1016/j.atmosenv.2019.116987](https://doi.org/10.1016/j.atmosenv.2019.116987)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Zhou, H, Zhao, H, Li, M, Feng, Q, Qi, J, Shi, Z, Mao, H & Jin, T 2019, 'Primary particulate matter emissions and estimates of secondary organic aerosol formation potential from the exhaust of a China V diesel engine', *Atmospheric Environment*, vol. 218, 116987. <https://doi.org/10.1016/j.atmosenv.2019.116987>

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1 **Primary particulate matter emissions and estimates of secondary**
2 **organic aerosol formation potential from the exhaust of a China V**
3 **diesel engine**

4 Hua Zhou^{a,c}, Hongwei Zhao^a, Jie Hu^b, Mengliang Li^c, Qian Feng^c,
5 Jingyu Qi^b, Zongbo Shi^d, Hongjun Mao^b, Taosheng Jin^{b*}

6 a. School of mechanical and aerospace engineering, Jilin University, Changchun 130022, P. R.
7 China

8 b. Center for Urban Transport Emission Research, State Environmental Protection Key Laboratory
9 of Urban Ambient Air Particulate Matter Pollution Prevention and Control, College of
10 Environmental Science and Engineering, Birmingham-Nankai Joint Research Institute, Nankai
11 University, Tianjin 300071, P. R. China

12 c. China Automotive Research and Technology Center Co. Ltd, Tianjin 300162, P. R. China

13 d. School of Geography Earth and Environmental Sciences, the University of Birmingham,
14 Birmingham, B15 2TT, UK

15 * Corresponding authors, E-mail address: jints@nankai.edu.cn (T. Jin)

16
17 **Abstract**

18 Vehicle emissions contribute to ambient particulate matter (PM) pollution directly
19 via emissions of PM and indirectly by secondary aerosol formation, as a result of trace
20 gas emissions. In this paper, we determined the emission factors of primary pollutants
21 and estimated the secondary organic aerosol (SOA) formation potential of a China V
22 heavy-duty diesel engine tested under ETC (European Transient Cycle) and ESC
23 (European Stationary Cycle) and different types of fuels with an engine dynamometer.
24 Volatile organic compounds (VOCs) emission factors were 55.7~121 mg/kwh, while
25 primary PM emission factors were 15.0~26.8 mg/kwh. These are substantially lower
26 than older diesel vehicles that meet pre-China V standards. Based on the SOA yields of
27 the measured VOCs, the SOA formation potential of diesel engines were estimated to
28 be 2.8~15.9 mg/kg fuel. The ratios of potential SOA / primary PM ranged from 0.07 to

29 0.16. We further showed that VOCs emission factors, SOA formation potential and the
30 ratios of SOA/ primary PM were highly dependent on test cycles, whereas the primary
31 PM emission factors on both test cycles and fuel quality.

32

33 *Keywords:* Vehicle emission; Secondary organic aerosol; Diesel particulate matter;
34 Volatile organic compounds; Driving test cycles; Fuel quality

35

36 **1 Introduction**

37 With more than 1.6 billion vehicles globally, Vehicle exhaust contributes
38 substantially to particulate matter with aerodynamic diameter less than 2.5 μm ($\text{PM}_{2.5}$)
39 in urban agglomerations (Chen et al., 2012, Cui et al., 2015, Gentner et al., 2017). $\text{PM}_{2.5}$
40 has important impacts on climate and human health by causing radiative force,
41 respiratory and cardiopulmonary diseases (Liu et al., 2015; Lelieveld et al., 2015).
42 Diesel vehicles contribute significantly to the particulate air pollution burden. In China,
43 diesel vehicles contribute more than 90% of primary PM emitted from vehicles,
44 although they only account for 9.4% of China's on-road vehicle population (MEE,
45 2018a).

46 $\text{PM}_{2.5}$ comprises a complex mixture of burned and unburned organic matter (OM)
47 from fuel and lubrication oil, elemental carbon (EC), sulfate, nitrate, ash and others
48 (Kittelson, 1998). Organic matter is mostly present in the form of organic aerosols.
49 Organic aerosols consist of primary organic aerosol (POA) and secondary organic
50 aerosol (SOA). POA is the OA emitted directly into the atmosphere; SOA is formed
51 from gas-phase oxidation, heterogeneous reactions on aerosol surfaces, and multiphase
52 chemistry of gas-phase organic compounds (Donahue et al., 2009; Hallquist et al., 2009).

53 SOA could be measured in smog chamber (Suarez-Bertoa et al., 2015) or estimated
54 by models (Zhang et al., 2017). Many studies have been carried out to estimate the SOA
55 formation of the Volatile organic compounds (VOCs) emitted from anthropogenic and
56 biogenic sources (Donahue et al., 2009; Feng et al., 2019). Vehicle emission was one of
57 the important anthropogenic sources (Gentner et al., 2012; Gordon et al., 2014a, b;

58 Huang et al., 2015). There are some existing models to estimate SOA formation
59 potential, such as fractional aerosol coefficients (FAC), secondary organic aerosol
60 potential (SOAP), and SOA yield methods (e.g. Goldstein et al., 2007; Robinson et al.,
61 2007; de Gouw et al., 2011). The FAC method estimates SOA formation potential using
62 reported FAC values (the ratio of the aerosol yield from a specific compound to its
63 initial concentration) (Grosjean, 1992) and the measured VOCs concentrations (Huang
64 et al., 2011). Wipawee et al. (2004) suggested that the main sources of anthropogenic
65 SOA precursor emissions in the Houston area should be point sources, mobile and area
66 sources which could be expected to be significant sources of SOA using FAC method.
67 The SOAP represents the SOA formation propensity of an organic compound when an
68 additional mass emission of that compound is added to the ambient atmosphere relative
69 to the SOA formed when the same mass of toluene is added (Derwent et al., 2010).
70 SOAPs are expressed as an index relative to toluene which is set to 100. SOA yield
71 methods use the yield for each SOA precursor (Gentner et al., 2012) to estimate SOA
72 formation potential. Zhang et al. (2017) concluded that, 27 VOCs were considered to
73 calculate the SOA concentration with SOA yield method (more than FAC and SOAP
74 methods), the assumption conditions of SOA yield method are closer to the real
75 conditions. Recently SOA yields of IVOCs (intermediate volatile organic compounds)
76 and SVOCs (semi volatile organic compounds) were considered important, and IVOCs
77 could dominate the SOA production from exhaust from diesel engines (Zhao et al., 2015,
78 Gentner et al., 2017).

79 Many previous studies indicated that vehicle emissions were important sources of
80 SOA precursors, but the relative importance of each vehicle type remained controversial
81 due to conflicting evidence. Historically, gasoline engines have been identified as the
82 major vehicle VOCs emissions (McDonald et al., 2015; Warneke et al., 2012), but
83 recently it has been found that the diesel contributes increasingly to overall VOCs
84 emissions (Bishop et al., 2008; Parrish et al., 2009; Gentner et al., 2017).

85 China V diesel vehicle emission standards were implemented in Beijing-Tianjin-
86 Hebei (Jing-Jin-Ji) since April 2016 and in the rest of China since Jan 2017. The stricter
87 standard required stricter after-treatment devices, such as DPF (Diesel Particulate

88 Filter), DOC (Diesel Oxidative Catalyst) and SCR (Selective catalytic reduction),
89 which could reduce primary vehicle emissions, but their influence on secondary
90 products still remained unknown. In addition, little data is available on the impact of
91 emission standard, fuel quality and driving cycle on primary emission and SOA
92 formation potential from China V diesel vehicles.

93 In this study, a heavy-duty diesel engine meeting China V was tested under
94 different test cycles and different types of fuels with an engine dynamometer. We first
95 estimated primary DPM (Diesel Particulate Matter) and VOCs emission factors. Then
96 the SOA yields of VOCs emissions under different conditions were presented to give
97 some preliminary discussions about the effects of fuel quality and driving cycle on SOA
98 formation potential. Finally, we calculated the ratios of SOA to primary DPM emission
99 factors. Results of our study quantified the primary and secondary PM pollution from
100 China V diesel emission, which could be helpful for vehicle emission and air quality
101 control policy.

102 **2 Materials and methods**

103 **2.1 Drive cycles**

104 Table 1 lists four dynamometer tests with YC6L280-50 diesel engine in this study.
105 There was only one replicate each of four different test conditions. The driving cycles
106 used in this study were ETC (European Transient Cycle) and ESC (European Stationary
107 Cycle). ETC include three modes, namely, urban driving, rural driving, and motorway
108 driving. The duration of each mode was 600s. ESC is a 13-mode, steady-state procedure.
109 The duration of each mode, Engine Speed, load and weight were determined. More
110 details of ETC and ESC are available online (Diesel Net, 2000a, b). Due to the use of a
111 single filter in each test, only the integrated result of all modes (ETC was 3-mode, ESC
112 was 13-mode) was reported. Fuels used in this study were China VI and China VI added
113 with detergent meeting the standard of GB T32859-2016(SAMR,2016). The contents
114 of the detergent were mainly Amine-containing high molecular compounds, which were
115 used to remove sediments and improve the efficiency of fuel atomization.

116 **2.2 Bench Test**

117 The test engine was mounted on a bench testing system (AVL, Graz, Austria) which
118 could perform both stationary and transient testing for engine emission measurement.
119 Detailed description of the testing system can be found in Jin et al. (2014). The engine
120 was tested on an engine dynamometer. The engine model was installed on many urban
121 buses in Tianjin, China in 2017. Table 2 lists the properties of the engine.

122 **2.3 DPM sampling and emission factor calculation**

123 In the engine dynamometer test, DPM was sampled with organic membrane filter
124 at $47 \pm 5^\circ\text{C}$. The diameter and porosity of membranes were 47 mm and $0.3 \mu\text{m}$
125 respectively. The filters were weighed before and after sampling. The measurement
126 uncertainty of weighing was 10^{-3} mg. Before weighing, the filters were stored in a room
127 with temperature of $25 \pm 5^\circ\text{C}$ and humidity of $45 \pm 5\%$ for 72 hours. The filters were
128 dark stored in a freezer with a set temperature of -19°C before extraction. Details about
129 sample analytical procedure were given in Jin et al. (2014).

130 Emission factors (EF) of DPM expressed in mg/kwh were estimated directly from
131 the sampling line after the dilution stage. The calculation of emission factor was carried
132 out as below (MEE, 2018b):

$$133 \quad EF_{PM} = \frac{PM_{mass}}{W_{act}} \quad (1)$$

$$134 \quad PM_{mass} = \frac{M_f}{M_{SAM}} \times \frac{M_{TOTW}}{1000} \quad (2)$$

135 Where EF_{PM} is the emission factor of PM in mg/kwh, PM_{mass} is the total PM
136 mass of each test in mg, W_{act} is the real power of engine in kwh, M_f is the total PM
137 mass on the filter in each test in mg, M_{TOTW} is the total mass of diluting gas in each
138 test in kg, M_{SAM} is the mass of diluting gas passing the filter in kg.

139 The emission factor of PM in mg/kg or mg/km was obtained on basis of fuel
140 consumption or travel distance instead of real power of engine.

141 **2.4 VOC Sampling and Analysis**

142 VOCs samples emitted from each test were collected after being diluted by 3.2 L
143 stainless steel SUMMA canisters (Entech Instruments Inc., USA) with a Teflon
144 connector. The samples collected in the Summa canisters were analyzed in a GC/MS
145 (7890A Gas Chromatograph System, 5975C VL Mass Spectrometer Detector, 7683B

146 Series Injector, Agilent Technologies), the detection limit, quantitative limit and
147 measured ranges of which were 6 ppb, 10 ppb and from 10 to 20000ppb, respectively.
148 Alkane, alkene and aromatic samples were pre-concentrated, and CO₂, H₂O, O₂, N₂ and
149 other interferents in the samples were removed by a triple module in a pre-concentration
150 system (Entech Model 7100) before the samples were injected into the GC/MS. The
151 carrier gas was helium. These canisters were cleaned in the laboratory following
152 USEPA method TO-14 through repeated evacuation and pressurization with high purity
153 nitrogen before sampling (USEPA, 1997).

154 In this study, quantitative detected VOCs were show in Table 3. Emission factor
155 of total VOCs was also calculated using the followed equation:

$$156 \quad EF_{VOC} = \frac{V\rho}{10^3 D_f W} \quad (3)$$

157 where EF_{VOC} is the emission factor of VOCs, in mg/kwh; V is the volume of
158 stainless-steel SUMMA canisters which equals 3.2 L in this study; ρ is the concentration
159 of VOCs samples in the SUMMA canisters, in $\mu\text{g}/\text{m}^3$; D_f is the dilution factor and
160 varied for each sampling; W is the total power, in kwh.

161 **2.5. Quality assurance (QA)/quality control (QC)**

162 The QA/QC protocol of the monitoring sequence was followed at all stages from
163 sample preparation to chemical analysis. Blank field filters were placed unopened next
164 to the samplers for the duration of sampling, after which they were returned to the
165 laboratory and treated as regular samples to ensure there was no significant back-
166 ground interference. A blank sample was run for each chemical analysis. Results
167 showed that all analyte concentrations in the blank organic membrane filters were less
168 than the method detection limits (MDL). All the fittings and tubing used by VOC
169 sampling were made of either stainless steel or polytetrafluoroethylene (PTFE) to
170 provide an inert sampling environment. Zero-air supply was used to dilute the exhaust
171 gas and was collected separately as field blank. No VOC was detected in the field blank.

172 **2.6 SOA Formation Potential Estimation**

173 The SOA formation potential emitted from the diesel engines is calculated based
174 on the SOA yields of the measured VOCs. We did not measure IVOCs and SVOCs and

175 thus the SOA estimation which represented the contribution was only from VOCs.
176 Measured VOCs are apportioned into five categories: aromatics, cycloalkanes,
177 branched alkanes, straight-chain alkanes, and alkenes. The SOA formation potential of
178 each category (P_{SOA} , g/kg fuel) is calculated by the following equations (Zhang et al.,
179 2017):

$$180 \quad SOA_j = \sum(Y_{i,j} \times VOC_{i,j}) \quad (4)$$

$$181 \quad P_{SOA} = \frac{\sum SOA_j}{M_{fuel}} \quad (5)$$

182 where j represents different categories of VOCs, i represents the number of carbons
183 in category j , SOA_j is the mass of SOA formed by VOCs of category j (g). $Y_{i,j}$ is the
184 yield of species i in category j (unitless), $VOC_{i,j}$ is the mass of SOA precursors of
185 species i in category j (g). Identified non-SOA precursors were excluded from total
186 VOC emissions. M_{fuel} is the mass of fuel consumed in one test in kg, P_{SOA} is the SOA
187 formation potential in one test in g/kg fuel.

188 The yields for each SOA precursor were referenced from Gentner et al. (2012),
189 which listed the high-NO_x SOA yields of known compounds using a combination of
190 measured SOA yields derived from laboratory-chamber experiments and approximate
191 SOA yields based on box modeling. For all compounds, high-NO_x SOA yields were
192 modeled assuming an average organic particle concentration of 10 $\mu\text{g}/\text{m}^3$, which was
193 used in chamber studies, urban areas and downwind urban areas (Gentner et al., 2012;
194 Chan et al., 2009; Zhang et al., 2007). In addition, the SOA yields of straight alkanes
195 increased by an average 16% in the range of 6-12 carbon atoms, C6–12 aromatics
196 increased by 19 % (Huang et al., 2015). Table 3 lists SOA yields in this study.

197 **3 RESULTS AND DISCUSSION**

198 **3.1 Total and speciated VOCs emission factors**

199 Figure 1 shows VOCs emission factors (mg/kg fuel) from diesel engines in this
200 study. Emission factor under ESC ranged from 108 to 115 mg/kg (or from 55.7 to 59.7
201 mg/kwh), which were significantly ($p=0.044$) lower than those under ETC (399 and
202 559 mg/kg or 87.7 and 121 mg/kwh). The results indicated that test cycles had a major

203 impact on the VOCs emission factors.

204 Figure 2 compares VOCs emission factors determined in this study with published
205 data. Our results (37.2~87.9 mg/km) were higher than those from a Euro V engine
206 (16.4~26.3 mg/km) reported by Lopes et al. (2014) but lower than those from China
207 II (120~456 mg/km) and China III (60~116 mg/km) by Yao et al. (2015a, b) and Pre-
208 Euro to Euro IV (191 to 1912mg/km) by Huang et al. (2015). This suggests that stricter
209 emission regulation significantly reduced VOCs emissions.

210 Propene and benzene were the two most abundant species of VOCs emitted from
211 the test engine, accounting for 39% and 13% of the total measured VOCs, respectively.
212 Wang et al. (2013) reported that ethylene (12%) was the most abundant VOCs followed
213 by toluene (11%) and benzene (8.8%) from light duty gasoline vehicles meeting China
214 III during ECE/EUDC test.

215 Figure 3 compares the composition of major categories of VOCs (including
216 alkanes, alkenes, alkynes and aromatics) in this study and those from other studies.
217 High proportions of alkenes were measured in the exhausts from test 1 and 3 (51% and
218 52%), which were higher than those in other studies. The VOC compositions of T2 and
219 T4 were similar to those by Huang et al. (2015).

220 **3.2 Primary PM emission factors**

221 Figure 1 also shows primary PM emission factors (mg/kg fuel) from the diesel
222 engine in this study. Emission factor under ESC ranged from 36.7 to 51.6 mg/kg (or
223 from 19 to 26.8 mg/kwh), while those under ETC condition were 69.2 and 110 mg/kg
224 (or 15 and 24.2 mg/kwh). There were some low-speed modes including idle in ESC,
225 and so the fuel consumption per kwh under ESC is higher than that under ETC. The
226 results also indicated that PM emission factors were dependent on both driving test
227 cycles and fuel quality.

228 Table 4 reports dynamometer results of China V diesel engine in this study and
229 other studies (in some studies, the primary PM emission factors were estimated as the
230 sum of BC and POA emission factors). Our results were close to those of Guo et al.
231 (2013), in which China V engine was used, but were slightly higher than those of

232 Georgios et al. (2012), where Euro V engine was used. On the other hand, our results
233 were lower than those of Gordon et al.(2014b), Chirico et al. (2010), Deng et al. (2017),
234 Huang et al. (2016) and He et al. (2015). These results suggest that the PM emission
235 factors of China V diesel engines in China become much lower.

236 **3.3 SOA formation potential**

237 Figure 1 also shows the SOA formation potential in 4 tests in this study. SOA
238 formation potential under ESC ranged from 2.8 to 3.6 mg/kg fuel (or from 1.4 to 1.9
239 mg/kwh), which were significantly ($p=0.062$) lower than those under ETC condition
240 (10.7 and 15.9 mg/kg or 2.3 and 3.5 mg/kwh). Due to the uncertainties of SOA yields,
241 there may be a large difference (even as much as twice) in the SOA formation potential.

242 In addition, the ratio of SOA formation potential of VOCs to primary PM
243 emissions were estimated. The ratios under ESC ranged from 0.07 to 0.08, which were
244 significantly lower than those under the ETC condition (0.15 and 0.16). The results
245 indicated that test cycles had a major impact on the SOA formation potential whereas
246 fuel quality had little impact.

247 Benzene, p-Ethyltoluene and methylbenzene were major precursor species,
248 accounting for 76%, 9.9% and 6.4% of the potential SOA, respectively. This is mainly
249 due to the very high yield of Benzene (Table 3), while the yield of propene was zero.
250 IVOCs were not measured in our study. Thus, the total SOA potential may be
251 significantly higher, potentially by an order of magnitude (Zhao et al., 2015; Huang et
252 al., 2018).

253 Figure 4 shows the comparison of our results and those from other studies. The
254 results of all other studies were measured in smog chambers, which were about a
255 magnitude higher than our results. Considering the absence of IVOCs and SVOCs
256 measurement in our study, our results are consistent with literature.

257 **4 CONCLUSIONS**

258 In this paper, a heavy-duty diesel engine was tested under different test cycles and
259 different types of fuels to estimate VOCs, PM emission factors and SOA formation
260 potential with an engine dynamometer.

261 VOCs emission factors were 55.7~121 mg/kwh, while primary PM emission
262 factors were 15~26.8 mg/kwh. As the engine emission standards were tightened in
263 China, the VOC and primary PM emission factors of diesel engines were reduced.
264 Based on the SOA yields of the measured VOCs, the SOA formation potential of diesel
265 engines were estimated and the results were 2.8~15.9 mg/kg fuel. Benzene, p-
266 Ethyltoluene and methylbenzene were major precursor species, accounting for 76%,
267 9.9% and 6.4% of the potential SOA, respectively. The ratios of SOA/ Primary PM
268 ranged from 0.07 to 0.16. Due to the absence of IVOCs measurement, the real SOA
269 formation potential and ratios of SOA/ Primary PM could be enlarged by about an order
270 of magnitude based on what others have observed for other diesel sources. The
271 differences of VOCs emission factors, SOA formation potential and ratios of SOA/
272 Primary PM were more affected by test cycle, while the differences of primary PM
273 emission factors were affected by both test cycle and fuel quality.

274 Results of our study shed light on the VOCs, primary PM and SOA formation
275 potential of diesel engines meeting China V emission standard, which were rarely
276 reported by other researchers. However, there are some uncertainties in these
277 estimations. More investigations are needed to validate the results observed in this study.
278 Future studies can pay more attention to some neglected components, such as IVOCs
279 and SVOCs.

280 **Acknowledgments**

281 This study was funded by the National Key Research and Development Program
282 of China (2017YFC0212100), National Natural Science Foundation of China (Grant
283 No. 21477057), International Clean Energy Talent Program 2017 of China Scholarship
284 Council (201702660024). We thank the editors and anonymous reviewers for their
285 valuable comments.

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Table 1 Design of four dynamometer tests

Test	Drive cycle	Aftertreatment	Fuel
T1	ESC	SCR	China VI ^a
T2	ESC	SCR	China VI
T3	ETC	SCR	China VI ^a
T4	ETC	SCR	China VI

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a. Added with detergent.

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Table 2 Properties of the diesel engines

Item	YC6L280-50
Structure	Turbocharged 6 cylinder in line
Displacement(L)	8.424
Maximum power(kW)	206
Maximum torque (Nm)	1100
Minimum fuel consumption at full load(g/kWh)	≤198
Emission regulation	China V

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Table 4 Emission factors of primary PM from diesel engine in our and other studies.

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Reference	Emission regulation	Primary PM emission factors	
		mg /kg fuel	mg/kwh
This study	China V	36.7~110	15.0~26.8
Georgios et al. (2012)	Euro V		3.5~12.7
Guo et al. (2013)	China V		15.5~28.5
Gordon et al.(2014b)	Tier 2	578~1134	
Chirico et al. (2010)	Euro III	573~906	
Deng et al. (2017)	Euro III	354~1286	
Huang et al. (2016)	China III		32.3~92.7
He et al. (2015)	China I	1588~3980	
	China II	521~853	
	China III	188~633	

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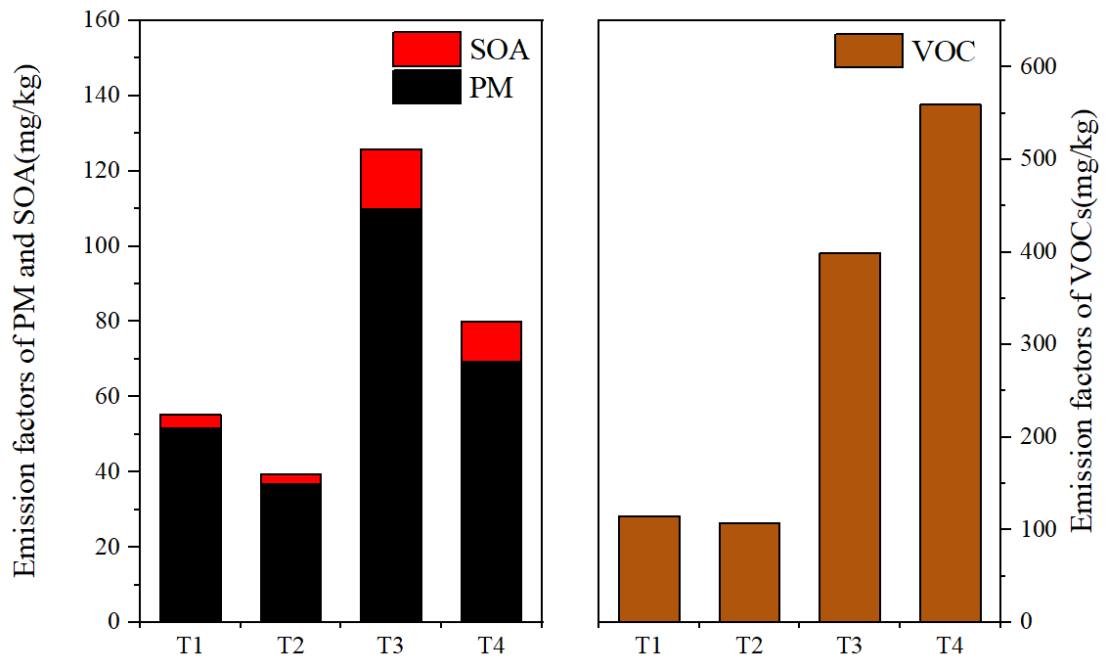
Table 3. Measured VOCs and their SOA yields in this study

VOCs	Category	Carbon Number	SOA yields
Acetone	ketone	3	
Dichloromethane	Haloalkane	1	
propene	Alkene	3	
Butane		4	
Hexane		6	
N-heptane		7	
n-Octane	Straight-chain	8	0.000696
n-Nonane	Alkanes	9	0.001392
Decane		10	0.003016
Undecane		11	0.006148
Dodecane		12	0.0116
Isobutane		4	
2-methylbutane	Branched Alkanes	5	
2,3-dimethylpentane		7	
3-methylhexane		7	
Cyclopentane		5	
Cyclohexane		6	0.0004±0.0003
Methylcyclopentane	Cycloalkanes	6	
Methylcyclohexane		7	0.0007±0.0006
2-methylheptane		8	0.0015±0.0011
benzene		6	0.167
Toluene		7	0.099
Ethylbenzene		8	
M-xylene	Aromatics	8	0.057
Styrene		8	
P-ethyltoluene		9	
M-ethyltoluene		9	0.092±0.068

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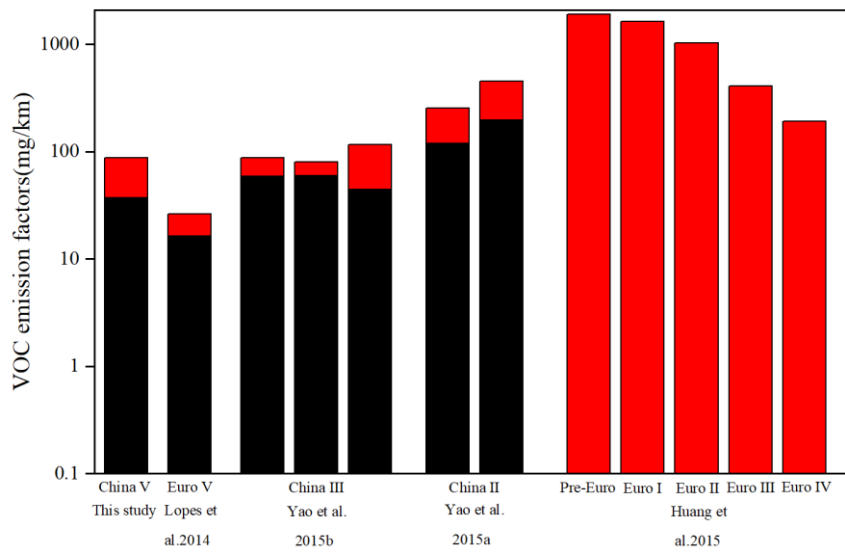


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Figure 1. Emission factors of potential SOA, primary PM and VOC

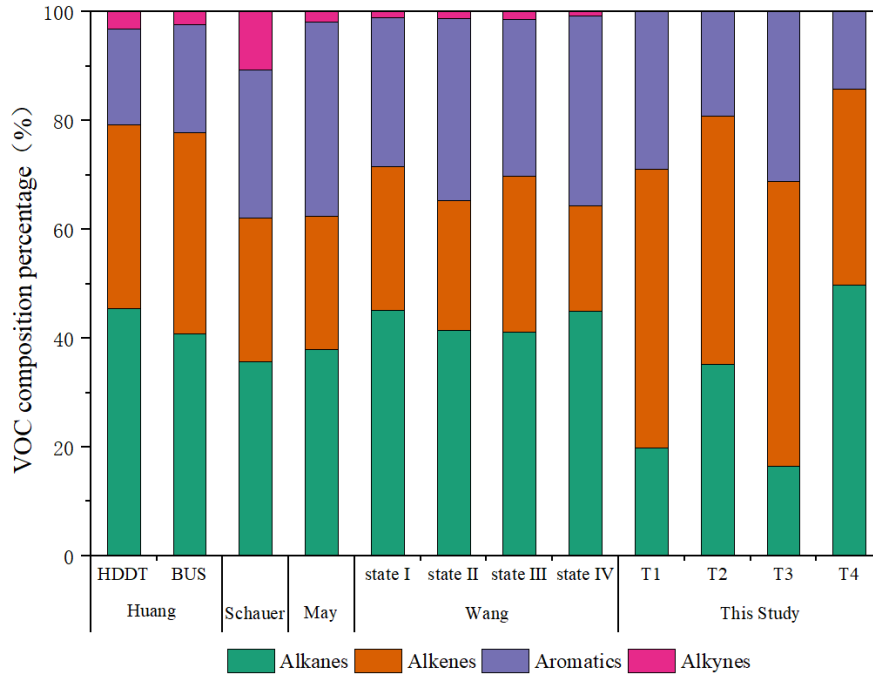


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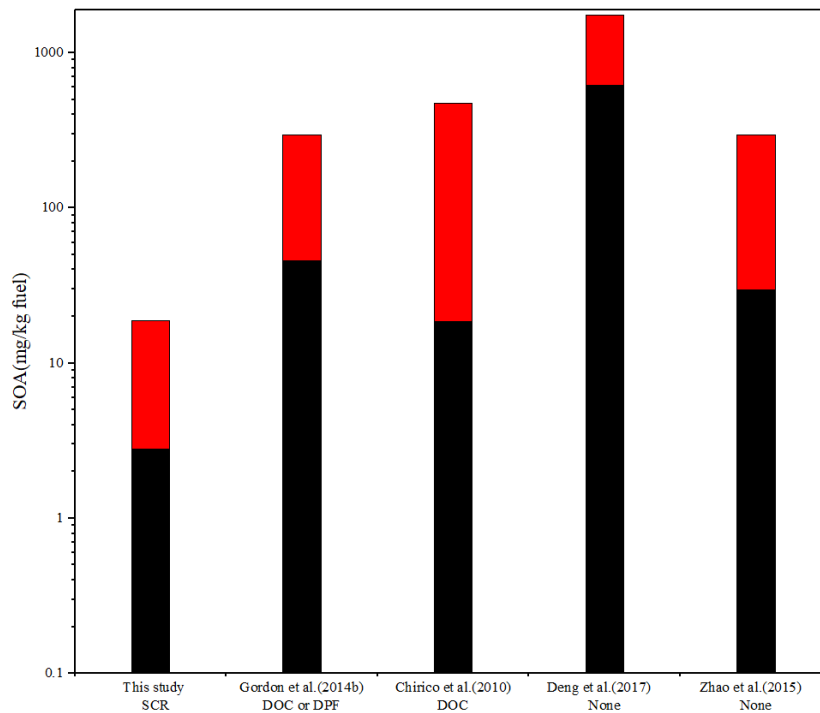
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Figure 2. VOC emission factors from diesel engines in our study and other studies



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Figure 3. VOC composition for each test comparing to other studies



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Figure 4. SOA from diesel engines in our study and other studies