

1 **Chemical and stable carbon isotopic composition of PM_{2.5} from**
2 **on-road vehicle emissions in the PRD region and implication for**
3 **vehicle emission control policy**

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19 **Abstract**

20 Vehicle emission is a major source of urban air pollution. In recent decade, the
21 Chinese government has introduced a range of policies to reduce the vehicle emission.
22 In order to understand the chemical characteristics of PM_{2.5} from on-road vehicle
23 emission in the Pearl River Delta (PRD) region and to evaluate the effectiveness of
24 control policies on vehicles emission, the emission factors of PM_{2.5} mass, elemental
25 carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC),
26 water-soluble inorganic ions (WSII), metal elements, organic compounds and stable
27 carbon isotopic composition were measured in the Zhujiang Tunnel of Guangzhou,
28 the PRD region of China in 2013. Emission factors of PM_{2.5} mass, OC, EC, and
29 WSOC were 92.4, 16.7, 16.4, and 1.31 mg vehicle⁻¹ km⁻¹ respectively. Emission
30 factors of WSII were 0.016 (F⁻) ~ 4.17 (Cl⁻) mg vehicle⁻¹ km⁻¹, totally contributing
31 about 9.8% to the PM_{2.5} emission. The sum of 27 measured metal elements accounted
32 for 15.2% of the PM_{2.5} emission. Fe was the most abundant metal element, with an
33 emission factor of 3.91 mg vehicle⁻¹ km⁻¹. Emission factors of organic compounds
34 including n-alkanes, PAHs, hopanes, and steranes were 91.9, 5.02, 32.0 and 7.59 μg
35 vehicle⁻¹ km⁻¹, respectively. Stable carbon isotopic composition δ¹³C value was
36 measured and it was -25.0‰ on average. An isotopic fractionation of 3.2‰ was found
37 during fuel combustion. Compared with a previous study in Zhujiang Tunnel in year
38 2004, emission factors of PM_{2.5} mass, EC, OC, WSII except Cl⁻, and organic
39 compounds decreased by 16.0-93.4%, which could be attributed to emission control

40 policy from 2004 to 2013. However, emission factors of most of the metal elements
41 increased significantly, which could be partially attributed to the changes in motor oil
42 additives and vehicle conditions. There are no mandatory national standards to limit
43 metal content from vehicle emission, which should be a concern of the government. A
44 snapshot of the 2013 characteristic emission of $PM_{2.5}$ and its constituents from
45 on-road vehicular fleet in the PRD region retrieved from our study was found to be
46 useful for the assessment of past and future implementation of vehicle emission
47 control policy.

48

49 **Keywords:** Tunnel; $PM_{2.5}$; vehicle emission; emission factor; water-soluble organic
50 carbon; stable carbon isotope; PRD

51 1. Introduction

52 Vehicle emission is a major source of urban air pollution and it accounts for
53 approximately 14~ 50% of total fine particle mass in urban areas (Sheesley et al.,
54 2007; Wang et al., 2008; Yu et al., 2013). The environmental and health effects of
55 vehicle emission **have been our concern** during the last decades. Numerous studies
56 have been conducted to characterize vehicular particulate matter (PM) emission in
57 many countries, with respect to emission factors, chemical composition, and size
58 distribution (Chiang and Huang, 2009; Laschober et al., 2004; Pio et al., 2013). The
59 characteristics of vehicle emission in China were studied by tunnel experiments,
60 dynamometer tests or road monitoring (He et al., 2008; Jin et al., 2014; Song et al.,
61 2012). Because of the differences in fuel qualities, engine conditions, and operation
62 practices, the PM emission from vehicles varied from region to region and time to
63 time.

64 The Pearl River Delta (PRD) region is located in the southern coast of China,
65 noted for its rapid urbanization and industrialization in the last few decades, has
66 experienced serious atmospheric pollution. Vehicle emission accounts for
67 approximately 25-30% of total fine PM in the PRD region
68 (http://epaper.southcn.com/nfdaily/html/2014-01/03/content_7261687.htm). Peer
69 reviewed papers had reported emission factors and chemical characteristic of PM_{2.5}
70 from vehicle emission in the PRD region, by means of tunnel studies in Zhujiang
71 Tunnel (Guangzhou) and Wutong Tunnel (Shenzhen) (He et al., 2006; He et al., 2008;

72 Huang et al., 2006b). However, the sampling in these studies was conducted in 2004.
73 During the past decade, the Environment Protect Agency of Guangdong Province
74 revised the “Motor vehicle exhaust pollution prevention and control regulations of
75 Guangdong Province” in 2008 and released the “PRD Regional Air Quality
76 Management Plan” and “A Clean Air Plan” in 2010, to improve the relevant air
77 quality through policies and measures. The emission standards for newly registered
78 vehicles were tightened to China IV and the better quality of gasoline and diesel were
79 supplied in 2013. Therefore, the characteristics of PM emission from vehicles in the
80 PRD region might have changed throughout these years.

81 Tunnel experiments and chassis dynamometer tests were widely used to measure
82 various pollutants emitted from vehicles (He et al., 2006; Heeb et al., 2003). However,
83 dynamometer test has the defect that it can not account for vehicle fleet composition
84 and emissions characteristics related to break and tire wear and re-suspension of road
85 dust (Thorpe and Harrison, 2008). Tunnel studies have been demonstrated to be a
86 suitable setup to measure PM emissions from on-road mixed fleets (Chiang and
87 Huang, 2009; Laschober et al., 2004; Pio et al., 2013).

88 This study was carried out in a roadway tunnel located in the PRD region. We
89 report here the emission factors of PM_{2.5} mass, organic carbon (OC), elemental carbon
90 (EC), water-soluble inorganic ions (WSII), metal elements, water-soluble organic
91 carbon (WSOC), organic compounds and stable carbon isotope. WSOC has the
92 potential to modify the hygroscopicity of particles, PM size and cloud condensation

93 nuclei activities (Shulman et al., 1996), but it is often ignored in previous studies
94 owing to the hydrophobic nature of the organic aerosol from primary vehicle emission.
95 Stable carbon isotope ($\delta^{13}\text{C}$) is very useful for tracing sources (Lopez-Veneroni, 2009;
96 Widory, 2006), and it was also less reported for vehicular exhaust emissions (Ancelet
97 et al., 2011; Widory, 2006). The objectives of this study are: (1) to obtain
98 comprehensive information on the chemical and stable carbon isotopic composition of
99 $\text{PM}_{2.5}$ emission from on-road vehicles in the PRD region; (2) to compare our results
100 with the previous study conducted in the same tunnel in 2004; (3) to evaluate the
101 effectiveness of the implementation of vehicle emission control policies from 2004 to
102 2013 in the PRD region. *Although the fleet composition in this tunnel was probably
103 different from the vehicle composition in the PRD region, it does not affect the
104 conclusions in this paper.*

105

106 **2. Experimental**

107 ***2.1. Tunnel sampling***

108 $\text{PM}_{2.5}$ samples were collected during August 10 to 14, 2013 from the roadway
109 tunnel (Zhujiang Tunnel) located in Guangzhou City, China. It has two bores, each of
110 which has three lanes with traffic in the same direction, as shown in Fig. 1. Two
111 high-volume $\text{PM}_{2.5}$ samplers (GUV-15HBL1, Thermo, USA) were placed at a
112 distance of 75 m from the entrance and 75 m from the exit, respectively. The vehicle
113 speed in the Zhujiang Tunnel was 18 to 45 km h^{-1} , with an average vehicle speed of

114 33.4 km h⁻¹ during the sampling. The air samples were drawn at about 1.13 m³ min⁻¹
115 through the quartz fiber filters (QFFs, 20.3 cm×25.4 cm, Whatman). Other special
116 devices such as diffusion denuders and foam plugs were not used due to the
117 difficulties in applying these devices. Consequently, volatilization losses or
118 adsorption artifacts may occur on the filter for semi-volatile organic compounds
119 especially for the low molecular weight compounds because these compounds exhibit
120 high volatility (Kavouras et al., 1999). However, the calculation of emission factors
121 were based on the concentration differences between the exit and entrance of the
122 tunnel, the potential losses or adsorption artifacts of semi-volatile organic compounds
123 would be partly deducted. Field blank samples were also collected by loading filters
124 into the samplers but without pulling air through. The ventilation system of the tunnel
125 was turned off during the sampling period, thus the dispersion of air pollutants in the
126 tunnel was mainly brought from the piston effect arising from the traffic flow. The
127 sampled filters were wrapped with annealed aluminum foil and stored in a refrigerator
128 at -40 °C till analysis. The meteorological parameters were synchronously recorded.
129 A video camera was placed at the exit to record the passing vehicles during the
130 sampling periods. The videotapes were then used to determine the vehicle counts and
131 to classify the vehicles into three categories, namely, diesel vehicles (DV)
132 (heavy-duty trucks, light-duty trucks and large passenger cars), gasoline vehicles (GV)
133 (small cars and motorcycles), and liquefied petroleum gas vehicles (LPGV) (bus and
134 taxies). The average traffic density during sampling was 1797 per hour with DV, GV

135 and LPGV proportion of $13.7 \pm 2.7\%$, $59.8 \pm 8.8\%$ and $26.5 \pm 7.9\%$ respectively.

136 More details of the vehicle counts and meteorological conditions are summarized in

137 Table S1 of the Supplement.

138

139 ***2.2 Chemical analysis***

140 The PM_{2.5} mass concentrations were determined gravimetrically by weighing the

141 quartz filters before and after sampling in an electronic [hygrothermostat](#) for 24 h at

142 25 °C and 50% relative humidity (RH). Then, samples were analyzed for OC/EC,

143 WSOC, WSII, metal elements, organic compounds and stable carbon isotope. The

144 experimental methods of the chemical analysis are available in the Supplement.

145

146 ***2.3 Calculation of emission factor***

147 Average emission factor (*EF*) was calculated for each sampling period on the

148 basis of the concentration difference between the exit and entrance of the tunnel by

149 the following equation (Handler et al., 2008):

$$EF = (C_{out} - C_{in})V/NL$$

150 where *EF* is the emission factor of a species in unit of mg vehicle⁻¹ km⁻¹, *N* is the

151 number of vehicles passing through the tunnel, *L* is the distance between inlet and

152 outlet sampling locations, *C_{out}* and *C_{in}* are the measured species concentration at the

153 tunnel outlet and inlet, respectively, and *V* is the corresponding air volume calculated

154 from the cross-sectional area of the tunnel, the average wind speed, and the sampling

155 duration of each filter. The average concentrations of all measured species at the inlet
156 and outlet sampling locations and the corresponding emission factors in this study are
157 presented in Tables S2-4 of the Supplement.

158

159 **3. Results and discussion**

160 *3.1 Characteristics of PM_{2.5} emissions from vehicles in the PRD region*

161 *3.1.1 PM_{2.5} mass, OC, EC, WSOC, WSII, metal elements*

162 The PM_{2.5} mass emission factors ranged from 79.8 to 107 mg vehicle⁻¹ km⁻¹,
163 with an average of 92.4 ± 8.9 mg vehicle⁻¹ km⁻¹. Average OC and EC emission factors
164 were 16.7±1.9 and 16.4±2.1 mg vehicle⁻¹ km⁻¹, respectively, and they accounted for
165 19 ± 2% and 18 ± 2% of PM_{2.5} mass emission. The ratio of OC to EC in the Zhujiang
166 Tunnel ranged from 0.77 to 1.35, with an average of 1.03. Previous studies have
167 shown that the OC/EC ratio is useful to separate gasoline engine emissions from
168 diesel emissions. Higher values (> 2) are associated with GV and LPGV exhaust, and
169 lower values (0.3 to ~0.9) associated with DV exhaust (Cadle et al., 1999; Cheng et
170 al., 2010; Gillies and Gertler, 2000). Therefore, the low OC/EC ratios in this study,
171 which are closer to that from DV exhaust, indicate that diesel vehicles played an
172 important role in the PM_{2.5} emission although the proportion of DV was only 13.7%
173 during the sampling. Additionally, it should be noted that emissions of EC from heavy
174 duty trucks are expected to be relatively low under the low speed operating conditions
175 in the tunnel (Kweon et al., 2002). Therefore, the ratio could be lower at the actual

176 driving condition of vehicle fleet with a higher speed on the road. The concentration
177 of WSOC in the inlet location was $6.21 \mu\text{g m}^{-3}$ (Table S2 of the Supplement) with a
178 percentage of 31.1% of OC, which is close to that of ambient air (Ding et al., 2008;
179 Ho et al., 2006). While in the outlet location, the concentration of WSOC was $8.00 \mu\text{g}$
180 m^{-3} , with a percentage of 17.9% of OC. The WSOC had been reported to contribute
181 on average 20% to OC in the exit of Marseille roadway tunnel (El Haddad et al.,
182 2009), in which background influence was included. The calculated emission factor of
183 WSOC in this study ranged from 0.5 to $2.8 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, with an average of 1.31
184 $\text{mg vehicle}^{-1} \text{ km}^{-1}$, which consisted of 7.84% of OC. Such a WSOC fraction is
185 considerably lower than that previously measured for biomass burning particles (71%)
186 (Mayol-Bracero et al., 2002). However, it could influence the hygroscopicity of
187 particles and the formation of secondary aerosols (Ho et al., 2006; Rogge et al., 1993b;
188 Weber et al., 2007) and is worthy of more attention and in-depth research.

189 The sum of WSII comprised about 9.8% of the $\text{PM}_{2.5}$ emission, with emission
190 factors of 4.17, 0.104, 0.609, 2.88, 0.165, 0.177 and $0.953 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ for Cl,
191 NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , Mg^{2+} and Ca^{2+} , respectively. The other WSII had a minor
192 contribution ($< 0.1 \text{ mg vehicle}^{-1} \text{ km}^{-1}$). Totally 27 measured metal elements
193 contributed 15.2% to the $\text{PM}_{2.5}$ emission. Fe was the most abundant element, with an
194 emission factor of $3.91 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, followed by Na $3.53 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, Al
195 $3.15 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, Ca $1.93 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, Mg $0.496 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, and K
196 $0.338 \text{ mg vehicle}^{-1} \text{ km}^{-1}$, which accounted for 4.2%, 3.8%, 3.4%, 2.1%, 0.5%, and 0.4%

197 of PM_{2.5} mass emission respectively. These six elements contributed 95.0% to the
198 total metal emission. Emission factors of other metals ranged from 0.0001 (Ag) to
199 0.25 (Ba) mg vehicle⁻¹ km⁻¹, with a sum of 0.71 mg vehicle⁻¹ km⁻¹. It is worth noting
200 that emission factors of elements including Na, K, Mg and Ca were significantly
201 higher than that of their corresponding water-soluble parts (see Table S3 of the
202 Supplement). The differences can be attributed to the water-insoluble matter with
203 these metal elements, such as calcium and magnesium carbonates and Na-K-Mg
204 bearing aluminosilicate species (Pio et al., 2013).

205 PM_{2.5} mass was also obtained by summing OM, EC, geological component, sea
206 salt, and major water soluble inorganic ions (NH₄⁺, SO₄²⁻, NO₃⁻). OC was multiplied
207 by 1.4 to estimate mass of OM (He et al., 2008). The geological component of 35 mg
208 vehicle⁻¹ km⁻¹ was estimated based on the Al emission data as present in Table S3 of
209 the Supplement. A typical road dust Al composition is 9% on average (Tiittanen et al.,
210 1999). Sea salt of 9 mg vehicle⁻¹ km⁻¹ was estimated by Na assuming sea salt contains
211 32% of Na. Thus, the average PM_{2.5} reconstructed mass was 91.8% of the
212 gravimetric value. This discrepancy can be attributed to the uncertainties in the
213 weighing process, the estimation methods and uncalculated components.

214

215 3.1.2 Organic compounds

216 The average emission factors and abbreviated names of 67 individual organic
217 compounds identified in the Zhujiang Tunnel, including n-alkanes, polycyclic

218 aromatic hydrocarbons (PAHs), hopanes, and steranes are listed in Table S4 of the
219 Supplement. These organic compounds accounted for 0.59% of the OM and 0.11% of
220 the PM_{2.5} mass emissions, The distributions of organic molecular markers associated
221 with PM_{2.5} are known to be source indicative despite of their small mass fractions
222 (Schauer et al., 1996; Simoneit, 1986). *n*-Alkanes are an important class of organic
223 compounds in atmospheric aerosols, and their homologue distribution may indicate
224 different pollution sources (Rogge et al., 1993a). In this study, the *n*-alkane traces
225 were dominated by C11-C36 with no odd-even carbon number predominance and the
226 maximum was at C24, consistent with the characteristics of vehicle emissions
227 reported by Simoneit (Simoneit, 1984, 1985). The emission factors of of individual
228 *n*-alkanes were in the range of 0.22 (C13)~ 13.3 (C24) $\mu\text{g vehicle}^{-1} \text{ km}^{-1}$ (Table S4 of
229 the Supplement).

230 There has been a worldwide concern to PAHs due to their known carcinogenic
231 and mutagenic properties. PAHs are thought to be the result of incomplete combustion.
232 Totally 15 priority PAHs (the results of naphthalene have not been discussed in this
233 study due to its low recovery) were identified and quantified. The emission factor of
234 total PAHs varied from 4.56 to 5.54 $\mu\text{g vehicle}^{-1} \text{ km}^{-1}$ in this study. The emission
235 factor of benzo[a]pyrene (BaP), which is often used as an indicator of PAHs and
236 regarded by World Health Organization as a good index for whole PAHs
237 carcinogenicity, was in the range of 0.37 to 0.46 $\mu\text{g vehicle}^{-1} \text{ km}^{-1}$. The emission
238 factors for other compounds ranged from 0.006 (acenaphthene) to 0.89 (pyrene) μg

239 vehicle⁻¹ km⁻¹ (Table S4 of the Supplement). Pyrene was the most abundant
240 compound, followed by chrysene (CHR), benzo[ghi]perylene (BghiP) and
241 benz[a]anthracene (BaA), which is different from biomass burning and coal
242 combustion (Huang et al., 2014; Shen et al., 2012). PAHs diagnostic ratios have been
243 used as a tool for identifying pollution emission sources including ANT/(ANT+PHE),
244 FLA/(FLA+PYR), BaA/(BaA+CHR), BbF/(BbF+BkF), IcdP/(IcdP+BghiP) and
245 BaP/(BaP+BghiP) (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002; Zhang et
246 al., 2005). We summarized PAHs ratios mentioned above in Fig. 2 for three
247 combustion sources including vehicle emission, biomass burning and coal combustion.
248 On the whole, the six ratios in this study are similar to the other tunnel experiments,
249 though environmental conditions of tunnels are different to some extent. It is also
250 suggested that the ratio of FLA/(FLA+PYR) and IcdP/(IcdP+BghiP) might be more
251 suitable to distinguish vehicle emission from biomass burning and coal combustion.

252 Hopanes and steranes are known molecular markers of aerosol emissions from
253 fossil fuel utilization (Simoneit, 1985). Rogge et al. (1993a) and Schauer et al. (1996)
254 had shown that these petroleum biomarkers can be used to trace motor vehicle
255 exhaust contributions to airborne PM in southern California atmosphere. Fourteen
256 major hopanes homologues with emission factors ranging from 0.46 ~ 9.14 µg
257 vehicle⁻¹ km⁻¹ and twelve steranes homologues ranging from 0.31 ~ 0.97 µg vehicle⁻¹
258 km⁻¹ were identified in this study. 17α(H),21β(H)-hopane (HP30) was the most
259 abundant component with the emission factor of 9.14 µg vehicle⁻¹ km⁻¹. The emission

260 factor of total hopanes was $32.0 \mu\text{g vehicle}^{-1} \text{ km}^{-1}$. Emissions of the S hopanes for the
261 extended $17\alpha(\text{H}),21\beta(\text{H})$ -hopane homologues > C31 were always higher than those of
262 the corresponding R pairs. All these characteristics of hopanes in the Zhujiang Tunnel
263 are consistent with those in gasoline and diesel exhausts (Rogge et al., 1993a;
264 Simoneit, 1985) and in other tunnel studies (see Fig. S1 of the Supplement). Emission
265 factors of individual sterane ranged from 0.31 to $0.97 \text{ ng vehicle}^{-1} \text{ km}^{-1}$, and the sum
266 of their emission factors was $7.58 \mu\text{g vehicle}^{-1} \text{ km}^{-1}$. The most abundant homologue
267 was C29 $\alpha\beta\beta$ -stigmastane (20R) (29 $\alpha\beta\beta$ R), followed by 29 $\alpha\alpha\alpha$ S and 29 $\alpha\beta\beta$ S.

268

269 3.1.3 Stable carbon isotope

270 Stable carbon isotope analysis of vehicle emissions in Zhujiang Tunnel yielded
271 $\delta^{13}\text{C}$ values ranging from -25.5 to -24.7‰ with an average value of $-25.0 \pm 0.2\text{‰}$, and
272 is comparable to previously reported ranges of -29 to -24.6‰ (Table 1) for vehicular
273 fuel emission. Generally, the variation in $\delta^{13}\text{C}_{\text{Fuel}}$ could affect the $\delta^{13}\text{C}$ of
274 hydrocarbons (Keppler et al., 2004; Yamada et al., 2009). In the PRD region, the $\delta^{13}\text{C}$
275 value of gasoline was on average $-28.6 \pm 0.6\text{‰}$, and the $\delta^{13}\text{C}$ value of diesel was $-$
276 $27.8 \pm 0.2\text{‰}$, and small variation of fuel $\delta^{13}\text{C}$ was observed (Hu et al., 2014). We
277 calculated the isotopic differences between $\delta^{13}\text{C}_{\text{PM}_{2.5}}$ and $\delta^{13}\text{C}_{\text{Fuel}}$, which represents
278 the apparent isotopic fractionation occurring during fuel burning. It expressed as
279 $\Delta^{13}\text{C}$ (‰), and is defined by the following equation (Yamada et al., 2009).

$$\Delta^{13}\text{C}_{\text{PM}_{2.5}\text{-Fuel}} = \left(\frac{\delta^{13}\text{C}_{\text{PM}_{2.5}} + 1000}{\delta^{13}\text{C}_{\text{Fuel}} + 1000} - 1 \right) \times 1000$$

280 In this study, the value of $\Delta^{13}\text{C}_{\text{PM}_{2.5}\text{-Fule}}$ was from 2.7 to 3.5 ‰, with an average
281 of 3.2 ‰, indicating an isotopic fractionation occurred during fuel combustion.
282 Comparing the stable isotopic carbon value of vehicular fuel emission with other
283 particulate emission sources (see Table 1), it is found that different emission sources
284 showed different stable carbon isotopic composition. For total carbon in PM_{2.5}
285 sample, $\delta^{13}\text{C}$ (‰) of coal and fuel oil combustion are -23.9‰ and -26.0‰
286 respectively, while that of vehicle emission is -25.9~-25.0‰. Obviously, the $\delta^{13}\text{C}$ (‰)
287 of vehicle emission is not significantly different from that of coal and fuel oil
288 combustion. However, they are obviously different from other sources, like dust
289 particle (-21~-18.4‰), C3 plant (-19.3~-13‰), and C4 plant (-34.7~-27‰). Therefore,
290 $\delta^{13}\text{C}$ might be used to distinguish the fossil fuel combustion from the other sources.

291

292 *3.2 Comparison with previous study conducted in the same tunnel*

293 To investigate the variation of chemical emission characteristics from vehicles in
294 the PRD region over the past decade, we compared the chemical emission
295 characteristics of this study with that of previous study (He et al., 2008) for the same
296 tunnel in 2004 (see Figs 3 and 4). Fig. 3 shows that PM_{2.5} mass, OC, EC decreased
297 significantly from 2004 to 2013. The reason can be partly attributed to the
298 implementation of pollution control measures for Chinese vehicle emission. During
299 this 9-year period, vehicle emission standard have raised two levels (from China II in
300 2004 to China IV in 2013) (Table 2). Additionally, comparing the fleet composition

301 of 2013 with 2004 in Zhujiang Tunnel, we found that the proportion of DV and GV
302 decreased while that of LPGV increased. LPG is a type of clean energy, and LPGV is
303 known to emit much less PM mass than GV and DV, while DV emits the most PM
304 mass (Allen et al., 2001; Myung et al., 2014; Yang et al., 2007). LPG could be
305 combusted more completely than gasoline and diesel. Changes mentioned above
306 contributed greatly to the decrease of emission factors of OC and EC (31.3% and
307 66.9%) and PM_{2.5} mass (16.0%) from 2004 to 2013. However, the emissions of PM_{2.5}
308 mass, OC and EC are still quite higher than those measured in other countries (see
309 Table S5 of the Supplement). The implication of these high emission levels is that
310 both the fuel quality and engine technologies in the PRD region need to be further
311 improved.

312 It is also found from Fig. 3 that emission factors of NO₃⁻, SO₄²⁻ and NH₄⁺
313 decreased from 2004 to 2013. Improvement of fuel quality resulted in sulfate
314 emission factor decrease from 3.18 to 0.61 mg vehicle⁻¹ km⁻¹, since the amount of
315 sulfur in fuel is slashed by 81.5~ 95 % in China IV (2013) when compared that in
316 China II (2004) (Table 3). The emission levels of nitrate and ammonium were about
317 one-tenth of those observed in 2004, possibly because NO_x emission standard is
318 tightened from 2004 to 2013 (Table 2) leading to the less production of ammonium
319 nitrate. Emission factor of chloride is quite higher than that obtained from Zhujiang
320 Tunnel in 2004 and other tunnels. Chloride was found up to 74 mg vehicle⁻¹ km⁻¹ in
321 PM₁₀ in the Howell Tunnel, due to the application of salt to melt ice on roadways in

322 the winter (Lough et al., 2005). However, it is not applicable in Guangzhou City. The
323 good correlation between Cl^- and Na^+ ($r^2=0.992$) indicates the re-suspension of sea
324 salt particles combined with vehicle emission PM might be a major source (He et al.,
325 2008).

326 Emission factors of most of the metal elements increased in Zhujiang Tunnel
327 from 2004 to 2013 except Cd and Pb. Na emission increased $3.18 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ in
328 2013 than in 2004. Na correlated weakly with Cl^- ($r^2=0.374$) and Na^+ ($r^2=0.429$). This
329 indicates that Na emission had other sources and it was not only from the
330 re-suspension of sea salt particles. The other four most abundant elements including
331 Fe, Ca, Mg, K increased by one to three times. As they are major components of
332 crustal material, resuspended road dust might result in their increase. However, the
333 wind speed in 2013 was found to be higher but not significantly than that in 2004 (3.8
334 m s^{-1} in 2013 versus 3.0 m s^{-1} in 2004). This minor difference in wind speed could not
335 account for the large increase. Furthermore, examination of the number of vehicles
336 per hour in 2013 and 2004 suggests that there were fewer vehicles per hour in 2013.
337 Therefore, a more plausible explanation is that there was a lot more dust on the road
338 in 2013. Other sources would cause the increased emissions of these elements, such as
339 oil additive (Mg, Ca, Cu, Zn. (Cadle et al., 1997)) and the wear of engines (Fe) (Cadle
340 et al., 1997; Garg et al., 2000), brakes and tires (Al, Fe, Cu, Mn, Cd, Ni, Pb and Zn.
341 (Garg et al., 2000; Pio et al., 2013)). Additionally, emissions of Zn, Cu, Mn, Cr, Ni, V,
342 As, Co, U, and Tl increased by 0.5 to 4.5 times. Although the sum of these elements

343 did not exceed 0.5% of PM_{2.5} mass, they are important for health effects. Lower
344 emission factor of Pb (0.01 ± 0.0007 mg vehicle⁻¹ km⁻¹) in 2013 than in 2004, could be
345 a result of the phase out of leaded gasoline across China in the late 1990s.

346 Figure 4 shows comparison of organic compounds emission in Zhujiang Tunnel
347 between 2004 and 2013. The *n*-alkane homologues exhibited a smooth hump-like
348 distribution with the most abundance at C24, as shown in Fig. 4a. Such a distribution
349 pattern was similar to patterns observed in Zhujiang Tunnel 2004. However, there are
350 some differences. Firstly, the highest abundant *n*-alkane shifted from C23 in 2004 to
351 C24 in 2013. This difference might be explained by the shift of gas-particle
352 partitioning as alkanes of < C26 are semi-volatile. However, a significant T-test ($p =$
353 0.14) showed that the temperatures were not significant different between this study
354 (33.0 ± 2.3 °C) and that in 2004 (31.8 ± 1.0 °C). Thus the differences due to different
355 C_{max} between this study and the study in 2004 can not be regarded as a result of
356 temperature differences. Furthermore, C_{max} was found to be C24 in every test of this
357 study, although the temperature ranged from 28.6 to 36.1 °C. It was reported that the
358 *n*-alkane in the highest abundance was C20 for DV and C25 or C26 for GV in
359 dynamometer tests (Rogge et al., 1993a; Schauer et al., 1999, 2002). As the emissions
360 collected in tunnel studies present a composite result of emissions from a mixed
361 vehicle fleet, the lower fraction of DV in 2013 was more likely the cause for the shift
362 of the C_{max}. Secondly, emission factors of C16-C26 in 2013 were quite lower than
363 those in 2004, while this trend reversed gradually after C27. Emission factors of the

364 PAHs decreased by 67.6% ~ 93.4%. BaP equivalents (BaP_{eq}) emission factors
365 decreased by 88.1% from 2004 to 2013 (Table S6 of the Supplement). This could be
366 attributed to the variation of fleet composition between 2004 and 2013. PAHs emitted
367 from LPGV are about one-third of that from GV (Yang et al., 2007), while DV emit
368 more PAHs than GV (Phuleria et al., 2006). Therefore, higher proportion of LPGV
369 and lower proportion of DV resulted in the lower emission factor of PAHs in 2013
370 than that in 2004. Emission factors of hopanes also decreased from 2004 to 2013, the
371 percentage of decrease ranged from 56.2% to 68.7%. However, the distributions of
372 hopane series derived from different tunnel studies were very similar (see Fig. S2 of
373 the Supplement). This seems to suggest that the hopane emission characteristics might
374 be independent of the fleet composition. This is a reasonable result given that hopanes
375 originate from the lubricating oil used in DV, GV and LPGV rather than from the fuel
376 (He et al., 2008; Phuleria et al., 2006). Owing to more units in heavy-duty vehicle
377 need lubrication, emission factors of hopanes attributable to heavy-duty vehicle were
378 higher than that to light-duty vehicle (Phuleria et al., 2006). Reduction of the
379 proportion of heavy-duty vehicle (bus, heavy-duty truck, large passenger cars)
380 proportion in fleet composition in 2013 (11.3%) compared that in 2004 (20%) might
381 be the reason that emission factors of hopanes decreased.

382

383 ***3.3 Implication for vehicle emission control policy***

384 Vehicle emission control strategies and policies adopted by Guangdong Province

385 can be classified as emission control on vehicles and fuel quality improvements or
386 alternative fuel utilization. The PM emission standards for newly registered vehicles
387 were tightened from China II in 2004 to China IV in 2013 (Table 2). The reduction of
388 on road high PM emitting vehicles, the phasing in of lower PM emitting vehicles, and
389 more environmental friendly vehicles on road with better advanced engines following
390 the implementation of these emission standards were effective for decreasing PM
391 emission. Emission factors of PM decreased by 16% from 2004 to 2013. Also for
392 NO_x, the emission limit was reduced to about half from 2004 to 2013. This change in
393 emission standard which limit NO_x emission was a major factor for emission factors
394 of nitrate and ammonium decreased by about 90%. On the other hand, National
395 Standard has been revised several times to improve fuel quality to adapt to stringent
396 vehicle emission standards (Table 3). Taken sulfur content as example, it has a sharp
397 decrease by over 90% from 2004 to 2013. The significant result is that emission
398 factors of sulfate decreased by 70%. Additionally, LPG and liquefied natural gas
399 (LNG) are gradually taking the place of diesel and gasoline as the fuel of taxi and bus
400 after 2004, and now seldom taxi and bus use diesel and gasoline as fuel
401 (<http://www.southcn.com/news/gdnews/nanyuedadi/200707040173.htm>). The
402 application of clean fuel led to closer complete combustion, and resulted in much less
403 emission from taxis and buses. In general, our results suggest that these strategies are
404 effective to reduce emission factors of PM_{2.5} mass, as well as OC, EC, WSII, and
405 organic compounds in PM_{2.5}. However, the total vehicle population increased year by

406 year. As shown in Fig. 5a, the total vehicle population increased by 49.1% from 2004
407 to 2013. Total emission of vehicle exhaust of PM_{2.5} mass (calculated as emission
408 factors multiply by annual average driving distance per car and vehicle population
409 (Wu et al., 2012)) increased by 25.2% from 2004 to 2013 (Fig. 5b). Consequently, we
410 have demonstrated that [more stringent emission standards and higher quality of fuel](#)
411 [or more utilization of clean fuels will be necessary to offset the impacts on the growth](#)
412 [in vehicle population and to improve air quality in the PRD region. Additionally,](#)
413 [owing to no mandatory national standards to limit metal content from vehicle](#)
414 [emission, the emission of most metal increased from 2004 to 2013](#) (Fig. 3 and 5b). In
415 China, heavy metals, including As, Cr, Cu, Ni and Tl, had been listed as key
416 substances that should be preferentially monitored in the atmospheric environment
417 (SEPA, 2003). These increases of metal elements should raise the awareness of the
418 government due to their health concern.

419

420 **4. Conclusions**

421 PM_{2.5} samples were collected between August 10 and 14, 2013 in Guangzhou
422 Zhujiang Tunnel to acquire a comprehensive snapshot of the chemical characteristics
423 of vehicle emission. The average emission factors of PM_{2.5} mass, EC, OC, WSOC,
424 WSII, metal elements, organic compounds and stable carbon isotope were measured.
425 Stable carbon isotope $\delta^{13}\text{C}$ value indicates an isotopic fractionation of 3.2‰ occurred
426 during fuel combustion. Compared with a previous study in Zhujiang Tunnel in year

427 2004, emission factors of PM_{2.5} mass, EC, OC, and major WSII decreased due to
428 control policy induced changes throughout the nine years from 2004 to 2013, that is,
429 change of fleet composition, implementation of more stringent gasoline and diesel
430 emission standards, improvement in fuel quality, and clean fuel used for taxi and
431 buses. The shift in n-alkanes distribution and decreased PAHs emission were due to
432 the lower proportion of DV in 2013 than in 2004, and the decrease in emission factor
433 of hopanes were due to the reduction of proportion of heavy duty vehicles. Our study
434 shows that control policies for vehicles emission by the government were effective to
435 decrease the emission factors of PM_{2.5}, EC, OC, and WSII from on-road vehicular
436 fleets. However, the increase in emission of most metal elements should raise the
437 awareness of the government, since metal elements, especially heavy metals could
438 affect human health. Also, to offset the impacts in the growth of vehicle population
439 and to improve air quality in the PRD region, more stringent emission and aggressive
440 control policies are necessary.

441

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449 **References**

- 450 Allen, J. O., Mayo, P. R., Hughes, L. S., Salmon, L. G., and Cass, G. R.: Emissions of
451 size-segregated aerosols from on-road vehicles in the Caldecott Tunnel, *Environ.*
452 *Sci. Technol.*, 35, 4189-4197, 2001.
- 453 Ancelet, T., Davy, P. K., Trompeter, W. J., Markwitz, A., and Weatherburn, D. C.:
454 Carbonaceous aerosols in an urban tunnel, *Atmos. Environ.*, 45, 4463-4469,
455 2011.
- 456 Boutton, T. W.: Stable carbon isotope ratios of natural materials II, Atmospheric,
457 terrestrial, marine, and freshwater environments, in: *Carbon Isotope Techniques*,
458 Coleman D. C. and Fry B. Academic Press, San Diego, 173-186, 1991.
- 459 Cadle, S. H., Mulawa, P. A., Ball, J., Donase, C., Weibel, A., Sagebiel, J. C., Knapp,
460 K. T., and Snow, R.: Particulate emission rates from in use high emitting
461 vehicles recruited in Orange County, California, *Environ. Sci. Technol.*, 31,
462 3405-3412, 1997.
- 463 Cadle, S. H., Mulawa, P. A., Hunsanger, E. C., Nelson, K., Ragazzi, R. A., Barrett, R.,
464 Gallagher, G. L., Lawson, D. R., Knapp, K. T., and Snow, R.: Composition of
465 light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area,
466 *Environ. Sci. Technol.*, 33, 2328-2339, 1999.
- 467 Cheng, Y., Lee, S. C., Ho, K. F., Chow, J. C., Watson, J. G., Louie, P. K. K., Cao, J.
468 J., and Hai, X.: Chemically-speciated on-road PM_{2.5} motor vehicle emission
469 factors in Hong Kong, *Sci. Total Environ.*, 408, 1621-1627, 2010.
- 470 Chiang, H. L., and Huang, Y. S.: Particulate matter emissions from on-road vehicles
471 in a freeway tunnel study, *Atmos. Environ.*, 43, 4014-4022, 2009.
- 472 Ding, X., Zheng, M., Yu, L. P., Zhang, X. L., Weber, R. J., Yan, B., Russell, A. G.,
473 Edgerton, E. S., and Wang, X. M.: Spatial and seasonal trends in biogenic
474 secondary organic aerosol tracers and water-soluble organic carbon in the
475 southeastern United States, *Environ. Sci. Technol.*, 42, 5171-5176, 2008.
- 476 El Haddad, I., Marchand, N., Dron, J., Temime-Roussel, B., Quivet, E., Wortham, H.,
477 Jaffrezo, J. L., Baduel, C., Voisin, D., Besombes, J. L., and Gille, G.:
478 Comprehensive primary particulate organic characterization of vehicular exhaust
479 emissions in France, *Atmos. Environ.*, 43, 6190-6198, 2009.
- 480 Garg, B. D., Cadle, S. H., Mulawa, P. A., Groblicki, P. J., Laroo, C., and Parr, G. A.:
481 Brake wear particulate matter emissions, *Environ. Sci. Technol.*, 34, 4463-4469,
482 2000.
- 483 Gillies, J. A., and Gertler, A. W.: Comparison and evaluation of chemically speciated
484 mobile source PM_{2.5} particulate matter profiles, *J. Air Waste Manage.*, 50,
485 1459-1480, 2000.
- 486 Handler, M., Puls, C., Zbiral, J., Marr, I., Puxbaum, H., and Limbeck, A.: Size and
487 composition of particulate emissions from motor vehicles in the

488 Kaisermuhlen-Tunnel, Vienna, *Atmos. Environ.*, 42, 2173-2186, 2008.

489 He, L. Y., Hu, M., Huang, X. F., Zhang, Y. H., Yu, B. D., and Liu, D. Q.: Chemical
490 characterization of fine particles from on-road vehicles in the Wutong tunnel in
491 Shenzhen, China, *Chemosphere*, 62, 1565-1573, 2006.

492 He, L. Y., Hu, M., Zhang, Y. H., Huang, X. F., and Yao, T. T.: Fine particle
493 emissions from on-road vehicles in the Zhujiang Tunnel, China, *Environ. Sci.*
494 *Technol.*, 42, 4461-4466, 2008.

495 Heeb, N. V., Forss, A. M., Saxer, C. J., and Wilhelm, P.: Methane, benzene and alkyl
496 benzene cold start emission data of gasoline-driven passenger cars representing
497 the vehicle technology of the last two decades, *Atmos. Environ.*, 37, 5185-5195,
498 2003.

499 Ho, K. F., Ho, S. S. H., Lee, S. C., Cheng, Y., Chow, J. C., Watson, J. G., Louie, P. K.
500 K., and Tian, L.: Emissions of gas- and particle-phase polycyclic aromatic
501 hydrocarbons (PAHs) in the Shing Mun Tunnel, Hong Kong, *Atmos. Environ.*,
502 43, 6343-6351, 2009.

503 Ho, K. F., Lee, S. C., Cao, J. J., Li, Y. S., Chow, J. C., Watson, J. G., and Fung, K.:
504 Variability of organic and elemental carbon, water soluble organic carbon, and
505 isotopes in Hong Kong, *Atmos. Chem. Phys.*, 6, 4569-4576, 2006.

506 Hu, P., Wen, S., Liu, Y. L., Bi, X. H., Chan, L. Y., Feng, J. L., Wang, X. M., Sheng,
507 G. Y., and Fu, J. M.: Carbon isotopic characterization of formaldehyde emitted
508 by vehicles in Guangzhou, China, *Atmos. Environ.*, 86, 148-154, 2014.

509 Huang, L., Brook, J. R., Zhang, W., Li, S. M., Graham, L., Ernst, D., Chivulescu, A.,
510 and Lu, G.: Stable isotope measurements of carbon fractions (OC/EC) in
511 airborne particulate: A new dimension for source characterization and
512 apportionment, *Atmos. Environ.*, 40, 2690-2705, 2006a.

513 Huang, W., Huang, B., Bi, X. H., Lin, Q. H., Liu, M., Ren, Z. F., Zhang, G. H., Wang,
514 X. M., Sheng, G. Y., and Fu, J. M.: Emission of PAHs, NPAHs and OPAHs
515 from residential honeycomb coal briquette combustion, *Energ. Fuel.*, 28,
516 636-642, 2014.

517 Huang, X. F., Yu, J. Z., He, L. Y., and Hu, M.: Size distribution characteristics of
518 elemental carbon emitted from Chinese vehicles: Results of a tunnel study and
519 atmospheric implications, *Environ. Sci. Technol.*, 40, 5355-5360, 2006b.

520 Jin, T. S., Qu, L., Liu, S. X., Gao, J. J., Wang, J., Wang, F., Zhang, P. F., Bai, Z. P.,
521 and Xu, X. H.: Chemical characteristics of particulate matter emitted from a
522 heavy duty diesel engine and correlation among inorganic and PAH components,
523 *Fuel*, 116, 655-661, 2014.

524 Kavouras, I. G., Lawrence, J., Koutrakis, P., Stephanou, E. G., and Oyola, P.:
525 Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in
526 Santiago de Chile: source reconciliation and evaluation of sampling artifacts,
527 *Atmos. Environ.*, 33, 4977-4986, 1999.

528 Kawashima, H., and Haneishi, Y.: Effects of combustion emissions from the Eurasian
529 continent in winter on seasonal delta C-13 of elemental carbon in aerosols in

530 Japan, *Atmos. Environ.*, 46, 568-579, 2012.

531 Keppler, F., Kalin, R. M., Harper, D. B., McRoberts, W. C., and Hamilton, J. T. G.:
532 Carbon isotope anomaly in the major plant C-1 pool and its global
533 biogeochemical implications, *Biogeosciences*, 1, 123-131, 2004.

534 Kweon, C. B., Foster, D. E., Schauer, J. J., and Okada, S.: Detailed chemical
535 composition and particle size assessment of diesel engine exhaust, *SAE*
536 *Technical Paper Series*, No. 2002-01-2670, doi:10.4271/2002-01-2670, 2002.

537 Laschober, C., Limbeck, A., Rendl, J., and Puxbaum, H.: Particulate emissions from
538 on-road vehicles in the Kaisermühlen-tunnel (Vienna, Austria), *Atmos. Environ.*,
539 38, 2187-2195, 2004.

540 Lopez-Veneroni, D.: The stable carbon isotope composition of PM_{2.5} and PM₁₀ in
541 Mexico City Metropolitan Area air, *Atmos. Environ.*, 43, 4491-4502, 2009.

542 Lough, G. C., Schauer, J. J., Park, J. S., Shafer, M. M., Deminter, J. T., and Weinstein,
543 J. P.: Emissions of metals associated with motor vehicle roadways, *Environ. Sci.*
544 *Technol.*, 39, 826-836, 2005.

545 Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari,
546 S., Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds
547 in biomass burning aerosols over Amazonia - 2. Apportionment of the chemical
548 composition and importance of the polyacidic fraction, *J. Geophys. Res.*,
549 107(D20), 8091, doi:10.1029/2001JD000522, 2002.

550 Myung, C. L., Ko, A., Lim, Y., Kim, S., Lee, J., Choi, K., and Park, S.: Mobile source
551 air toxic emissions from direct injection spark ignition gasoline and LPG
552 passenger car under various in-use vehicle driving modes in Korea, *Fuel Process.*
553 *Technol.*, 119, 19-31, 2014.

554 Oda, J., Nomura, S., Yasuhara, A., and Shibamoto, T.: Mobile sources of atmospheric
555 polycyclic aromatic hydrocarbons in a roadway tunnel, *Atmos. Environ.*, 35,
556 4819-4827, 2001.

557 Phuleria, H. C., Geller, M. D., Fine, P. M., and Sioutas, C.: Size-resolved emissions
558 of organic tracers from light-and heavy-duty vehicles measured in a California
559 roadway tunnel, *Environ. Sci. Technol.*, 40, 4109-4118, 2006.

560 Pio, C., Mirante, F., Oliveira, C., Matos, M., Caseiro, A., Oliveira, C., Querol, X.,
561 Alves, C., Martins, N., Cerqueira, M., Camoes, F., Silva, H., and Plana, F.:
562 Size-segregated chemical composition of aerosol emissions in an urban road
563 tunnel in Portugal, *Atmos. Environ.*, 71, 15-25, 2013.

564 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.:
565 Sources of Fine Organic Aerosol .2. Noncatalyst and Catalyst-Equipped
566 Automobiles and Heavy-Duty Diesel Trucks, *Environ. Sci. Technol.*, 27,
567 636-651, 1993a.

568 Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., and Simoneit, B. R. T.:
569 Quantification of Urban Organic Aerosols at a Molecular-Level - Identification,
570 Abundance and Seasonal-Variation, *Atmos. Environ. A-Gen.*, 27, 1309-1330,
571 1993b.

572 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of
573 emissions from air pollution sources. 2. C-1 through C-30 organic compounds
574 from medium duty diesel trucks, *Environ. Sci. Technol.*, 33, 1578-1587, 1999.

575 Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of
576 emissions from air pollution sources. 5. C-1-C-32 organic compounds from
577 gasoline-powered motor vehicles, *Environ. Sci. Technol.*, 36, 1169-1180, 2002.

578 Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and
579 Simoneit, B. R. T.: Source apportionment of airborne particulate matter using
580 organic compounds as tracers, *Atmos. Environ.*, 30, 3837-3855, 1996.

581 SEPA: State Environmental Protection Administration, Air And Waste Gas Monitor
582 Analysis Method, China Environmental Science Press, Beijing, 2003.

583 Sheesley, R. J., Schauer, J. J., Chowdhury, Z., Cass, G. R., and Simoneit, B. R. T.:
584 Characterization of organic aerosols emitted from the combustion of biomass
585 indigenous to South Asia, *J. Geophys. Res.*, 108(D9), 4285,
586 doi:10.1029/2002JD002981, 2003.

587 Sheesley, R. J., Schauer, J. J., Zheng, M., and Wang, B.: Sensitivity of molecular
588 marker-based CMB models to biomass burning source profiles, *Atmos. Environ.*,
589 41, 9050-9063, 2007.

590 Shen, G. F., Tao, S., Wang, W., Yang, Y. F., Ding, J. N., Xue, M. A., Min, Y. J., Zhu,
591 C., Shen, H. Z., Li, W., Wang, B., Wang, R., Wang, W. T., Wang, X. L., and
592 Russell, A. G.: Emission of Oxygenated Polycyclic Aromatic Hydrocarbons
593 from Indoor Solid Fuel Combustion, *Environ. Sci. Technol.*, 45, 3459-3465,
594 2011.

595 Shen, G. F., Tao, S., Wei, S. Y., Zhang, Y. Y., Wang, R., Wang, B., Li, W., Shen, H.
596 Z., Huang, Y., Chen, Y. C., Chen, H., Yang, Y. F., Wang, W., Wang, X. L., Liu,
597 W. X., and Simonich, S. L. M.: Emissions of Parent, Nitro, and Oxygenated
598 Polycyclic Aromatic Hydrocarbons from Residential Wood Combustion in Rural
599 China, *Environ. Sci. Technol.*, 46, 8123-8130, 2012.

600 Shulman, M. L., Jacobson, M. C., Carlson, R. J., Synovec, R. E., and Young, T. E.:
601 Dissolution behavior and surface tension effects of organic compounds in
602 nucleating cloud droplets, *Geophys. Res. Lett.*, 23, 277-280, 1996.

603 Simoneit, B. R. T.: Organic-Matter of the Troposphere .3. Characterization and
604 Sources of Petroleum and Pyrogenic Residues in Aerosols over the Western
605 United-States, *Atmos. Environ.*, 18, 51-67, 1984.

606 Simoneit, B. R. T.: Application of Molecular Marker Analysis to Vehicular Exhaust
607 for Source Reconciliations, *Int. J. Environ. Anal. Chem.*, 22, 203-233, 1985.

608 Simoneit, B. R. T.: Characterization of Organic-Constituents in Aerosols in Relation
609 to Their Origin and Transport - a Review, *Int. J. Environ. Anal. Chem.*, 23,
610 207-237, 1986.

611 Song, S. J., Wu, Y., Jiang, J. K., Yang, L., Cheng, Y., and Hao, J. M.: Chemical
612 characteristics of size-resolved PM_{2.5} at a roadside environment in Beijing,
613 China, *Environ. Pollut.*, 161, 215-221, 2012.

614 Tanner, R. L., and Miguel, A. H.: Carbonaceous Aerosol Sources in Rio De Janeiro,
615 Aerosol Sci. Technol., 10, 213-223, 1989.

616 Thorpe, A., and Harrison, R. M.: Sources and properties of non-exhaust particulate
617 matter from road traffic: A review, Sci. Total Environ., 400, 270-282, 2008.

618 Tiittanen, P., Timonen, K. L., Ruuskanen, J., Mirme, A., and Pekkanen, J.: Fine
619 particulate air pollution, resuspended road dust and respiratory health among
620 symptomatic children, Eur Respir J, 13, 266-273, 1999.

621 Tobiszewski, M., and Namiesnik, J.: PAH diagnostic ratios for the identification of
622 pollution emission sources, Environ. Pollut., 162, 110-119, 2012.

623 Wang, H. L., Zhuang, Y. H., Wang, Y., Sun, Y., Yuan, H., Zhuang, G. S., and Hao, Z.
624 P.: Long-term monitoring and source apportionment of PM_{2.5}/PM₁₀ in Beijing,
625 China, J. Environ. Sci-China, 20, 1323-1327, 2008.

626 Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw,
627 J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E.: A
628 study of secondary organic aerosol formation in the anthropogenic-influenced
629 southeastern United States, J. Geophys. Res., 112, D13302,
630 doi:10.1029/2007JD008408, 2007.

631 Widory, D.: Combustibles, fuels and their combustion products: A view through
632 carbon isotopes, Combust. Theor. Model., 10, 831-841, 2006.

633 Widory, D., Roy, S., Le Moullec, Y., Goupil, G., Cocherie, A., and Guerrot, C.: The
634 origin of atmospheric particles in Paris: a view through carbon and lead isotopes,
635 Atmos. Environ., 38, 953-961, 2004.

636 Wu, Y. Y., Zhao, P., Zhang, H. W., Wang, Y., and Mao, G. Z.: Assessment for Fuel
637 Consumption and Exhaust Emissions of China's Vehicles: Future Trends and
638 Policy Implications, Sci. World J., 591343, 1-8, 2012.

639 Yamada, K., Hattori, R., Ito, Y., Shibata, H., and Yoshida, N.: Carbon isotopic
640 signatures of methanol and acetaldehyde emitted from biomass burning source,
641 Geophys. Res. Lett., 36, L18807, doi:10.1029/2009GL038962, 2009.

642 Yang, H. H., Chien, S. M., Cheng, M. T., and Peng, C. Y.: Comparative study of
643 regulated and unregulated air pollutant emissions before and after conversion of
644 automobiles from gasoline power to liquefied petroleum gas/gasoline dual-fuel
645 retrofits, Environ. Sci. Technol., 41, 8471-8476, 2007.

646 Yu, L. D., Wang, G. F., Zhang, R. J., Zhang, L. M., Song, Y., Wu, B. B., Li, X. F., An,
647 K., and Chu, J. H.: Characterization and Source Apportionment of PM_{2.5} in an
648 Urban Environment in Beijing, Aerosol Air Qual. Res., 13, 574-583, 2013.

649 Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and
650 Sylvestre, S.: PAHs in the Fraser River basin: a critical appraisal of PAH ratios
651 as indicators of PAH source and composition, Org. Geochem., 33, 489-515,
652 2002.

653 Zhang, X. L., Tao, S., Liu, W. X., Yang, Y., Zuo, Q., and Liu, S. Z.: Source
654 diagnostics of polycyclic aromatic hydrocarbons based on species ratios: A
655 multimedia approach, Environ. Sci. Technol., 39, 9109-9114, 2005.

656 Zhang, Y. X., Schauer, J. J., Zhang, Y. H., Zeng, L. M., Wei, Y. J., Liu, Y., and Shao,
657 M.: Characteristics of particulate carbon emissions from real-world Chinese coal
658 combustion, *Environ. Sci. Technol.*, 42, 5068-5073, 2008.
659

660 **Table 1.** $\delta^{13}\text{C}$ values (‰) of PM from vehicle emission in this study and other emission sources

Emission sources and Sampling site	Particle types	$\delta^{13}\text{C}$ values	Sampling time	Reference
Vehicular fuel emission				
Vehicle emissions (Zhujiang Tunnel, China)	PM _{2.5} /TC	-25.0±0.3	August 2013	This study
Vehicle emissions (Tunnel of Rio de Janeiro, Brazil)	PM/OC	-25.4	April 1985	(Tanner and Miguel, 1989)
Vehicle emissions (Tunnel of Rio de Janeiro, Brazil)	PM/EC	-24.8	April 1985	(Tanner and Miguel, 1989)
Complete combustion of diesel	PM/TC	-29	N/A	(Widory, 2006)
Complete combustion of gasoline	PM/TC	-27	N/A	(Widory, 2006)
Vehicle emissions (Cassier Tunnel, Canada)	PM _{2.5} /OC	-27.1	N/A	(Huang et al., 2006a)
Vehicle emissions (Cassier Tunnel, Canada)	PM _{2.5} /EC	-26.9	N/A	(Huang et al., 2006a)
Diesel vehicle emissions (Central Camionera del Norte, Mexico)	PM _{2.5} /TC	-24.6±0.3	March 2002	(Lopez-Veneroni, 2009)
Gasoline vehicle emissions (Tunnel of Avenida Chapultepec, Mexico)	PM _{2.5} /TC	-25.5±0.1	March 2002	(Lopez-Veneroni, 2009)
Vehicle emissions (Mount Victoria Tunnel, New Zealand)	PM _{2.5} /TC	-25.9±0.8	December 2008 to March 2009	(Ancelet et al., 2011)
Non-vehicular fuel sources				
Coal combustion (Paris, Franch)	PM _{2.5} /TC	-23.9±0.5	May to September 2002	(Widory et al., 2004)
Coal combustion (Yurihonjo City, Japan)	PM _{2.5} /EC	-23.3	N/A	(Kawashima and Haneishi, 2012)
Charcoal combustion (Yurihonjo City, Japan)	PM _{2.5} /EC	-27.4±1.7	N/A	(Kawashima and Haneishi, 2012)
Fireplace soot (Yurihonjo City, Japan)	PM/EC	-26.5±0.1	N/A	(Kawashima and Haneishi, 2012)
Fuel oil combustion (Paris, Franch)	PM _{2.5} /TC	-26.0±0.5	May to September 2002	(Widory et al., 2004)
Dust particles				
Street dust (Mexico City, Mexico)	PM _{2.5} /TC	-21±0.2	March 2002	(Lopez-Veneroni, 2009)
Street dust (Yurihonjo City, Japan)	PM _{2.5} /EC	-18.4~ -16.4	November 2009	(Kawashima and Haneishi, 2012)
Biomass burning				
C4 Plant	PM/TC	-13±4	N/A	(Boutton, 1991)
C4 Plant (Yurihonjo City, Japan)	PM _{2.5} /EC	-19.3~ -16.1	April to November 2009	(Kawashima and Haneishi, 2012)
C3 Plant	PM/TC	-27±6	N/A	(Boutton, 1991)
C3 Plant (Yurihonjo City, Japan)	PM _{2.5} /EC	-34.7~ -28.0	April to November 2009	(Kawashima and Haneishi, 2012)

661 **Table 2.** Vehicle emission standard and limit for PM and NO_x implemented in

662 Guangzhou after 2000

Emission standard	Year ^a	Limit for PM		Limit for NO _x	
		g km ^{-1 b}	g kWh ^{-1 c}	g km ^{-1 b}	g kWh ^{-1 c}
China I	2001	0.14~0.40	0.40~ 0.68	-	8.0~ 9.0
China II	2004	0.08~0.20	0.15	-	7.0
China III	2007	0.05~ 0.10	0.10~ 0.21	0.15~ 0.78	5.0
China IV	2010	0.025~0.060	0.02~ 0.03	0.08~ 0.39	3.5

663 ^a Year of implementation; ^b for light duty vehicle; ^c for compression ignition and gas fuelled positive ignition

664 engines of vehicles.

665 **Table 3.** Vehicle fuel standard and limit for sulfur content (mg kg^{-1}) implemented in
 666 Guangzhou after 2000

Standard	China I		China II		China III		China IV	
	Limit	Year ^a	Limit	Year	Limit	Year	Limit	Year
Gasoline	1000	2001	500	2005	150	2006	50	2010
Diesel	2000	2002	500	2003	350	2010	50	2013
LPG	-	-	270 ^b	2003	-	-	50	2013

667 ^a Year of implementation; ^b unit: mg m^{-3}

668 **Figure captions:**

669 **Fig. 1.** Sampling schematic diagram of the Zhujiang Tunnel.

670

671 **Fig. 2.** ANT/(ANT+PHE), FLA/(FLA+PYR), BaA/(BaA+CHR), BbF/(BbF+BkF),
672 BaP/(BaP+BghiP) and IcdP/(IcdP+BghiP) ratios for three source emissions. The
673 vehicle emission (VE) composition is from data collected in roadway tunnel((this
674 study), (He et al., 2008), (Ancelet et al., 2011), (He et al., 2006), (Ho et al., 2009),
675 (Oda et al., 2001). The biomass burning profiles are obtained from 9 straws (Shen et
676 al., 2011), 26 firewood (Shen et al., 2012), 3 plant leaves and branches (Sheesley et al.,
677 2003) and 2 biomass briquettes burning (Sheesley et al., 2003). The coal combustion
678 profiles are selected from 5 coals imitate combustion (Shen et al., 2011)and main
679 coal-mining regions in China (Zhang et al., 2008Zhang et al., 2008).

680

681 **Fig. 3.** Comparison of PM_{2.5}, OC, EC, WSII and metal emissions in the Zhujiang
682 Tunnel sampling in 2004 and 2013.

683

684 **Fig. 4.** Comparison of organic compounds emissions in the Zhujiang Tunnel sampling
685 in 2004 and 2013.

686

687 **Fig. 5.** (a) Growth in total vehicle population in Guangzhou during 2004-2013. (b)
688 Total exhaust emission of PM_{2.5} mass, OC, EC, WSII and metal in 2004 and 2013.