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

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Abstract

Vehicle emission is a major source of urban air pollution. In recent decade, the Chinese government has introduced a range of policies to reduce the vehicle emission. In order to understand the chemical characteristics of $PM_{2.5}$ from on-road vehicle emission in the Pearl River Delta (PRD) region and to evaluate the effectiveness of control policies on vehicles emission, the emission factors of $PM_{2.5}$ mass, elemental carbon (EC), organic carbon (OC), water-soluble organic carbon (WSOC), water-soluble inorganic ions (WSII), metal elements, organic compounds and stable carbon isotopic composition were measured in the Zhujiang Tunnel of Guangzhou, in the PRD region of China in 2013. Emission factors of $PM_{2.5}$ mass, OC, EC, and WSOC were 92.4, 16.7, 16.4, and 1.31 mg vehicle^{-1} km^{-1} respectively. Emission factors of WSII were 0.016 (F^-) ~ 4.17 (Cl^-) mg vehicle^{-1} km^{-1}, totally contributing about 9.8% to the $PM_{2.5}$ emission. The sum of 27 measured metal elements accounted for 15.2% of the $PM_{2.5}$ emission. Fe was the most abundant metal element, with an emission factor of 3.91 mg vehicle^{-1} km^{-1}. Emission factors of organic compounds including n-alkanes, PAHs, hopanes, and steranes were 91.9, 5.02, 32.0 and 7.59 μg vehicle^{-1} km^{-1}, respectively. Stable carbon isotopic composition $\delta^{13}C$ value was measured and it was -25.0‰ on average. An isotopic fractionation of 3.2‰ was found during fuel combustion. Compared with a previous study in Zhujiang Tunnel in year 2004, emission factors of $PM_{2.5}$ mass, EC, OC, WSII except Cl^-, and organic compounds decreased by 16.0-93.4%, which could be attributed to emission control

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

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

1. Introduction

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

Pearl River Delta (PRD) region, located in the southern coast of China has experienced serious atmospheric pollution with its rapid urbanization and industrialization in the last few decades. Vehicle emission accounts for approximately 25-30% of total fine PM in the PRD region (http://epaper.southcn.com/nfdaily/html/2014-01/03/content_7261687.htm). Peer reviewed papers had reported emission factors and chemical characteristic of $PM_{2.5}$ from vehicle emission in the PRD region, by means of tunnel studies in Zhujiang 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 cannot 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), however, it is often ignored in previous
94 studies owing to the hydrophobic nature of the organic aerosol from primary vehicle
95 emission. Stable carbon isotope ($\delta^{13}C$) is very useful for tracing sources
96 (Lopez-Veneroni, 2009; Widory, 2006), and it was also less reported for vehicular
97 exhaust emissions (Ancelet et al., 2011; Widory, 2006). The objectives of this study
98 are: (1) to obtain comprehensive information on the chemical and stable carbon
99 isotopic composition of $PM_{2.5}$ emission from on-road vehicles in the PRD region; (2)
100 to compare our results with the previous study conducted in the same tunnel in 2004;
101 (3) to evaluate the effectiveness of the implementation of vehicle emission control
102 policies from 2004 to 2013 in the PRD region. Although the fleet composition in this
103 tunnel was probably different from the vehicle composition in the PRD region, it does
104 not affect the conclusions in this paper.
105

106 **2. Experimental**

107 ***2.1. Tunnel sampling***

108 $PM_{2.5}$ 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 $PM_{2.5}$ 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 PM samples were collect at about 1.13 m^3 min^{-1}
115 through the quartz fiber filters (QFFs, 20.3 cm×25.4 cm, Whatman). Other devices
116 such as diffusion denuders and foam plugs were not used due to the difficulties in
117 applying these devices. Consequently, volatilization losses or adsorption artifacts may
118 occur on the filter for semi-volatile organic compounds especially for the low
119 molecular weight compounds due to their high volatility (Kavouras et al., 1999).
120 However, the calculation of emission factors was based on the concentration
121 differences between the exit and entrance of the tunnel, the potential losses or
122 adsorption artifacts of semi-volatile organic compounds would be partly deducted.
123 Field blank samples were also collected by loading filters into the samplers but
124 without pulling air through. The ventilation system of the tunnel was turned off during
125 the sampling period, thus the dispersion of air pollutants in the tunnel was mainly
126 brought from the piston effect arising from the traffic flow. The sampled filters were
127 wrapped with annealed aluminum foil and stored in a refrigerator at −40 °C till
128 analysis. The meteorological parameters were synchronously recorded. A video
129 camera was placed at the exit to record the passing vehicles during the sampling
130 periods. The videotapes were then used to determine the vehicle counts and to classify
131 the vehicles into three categories, namely, diesel vehicles (DV) (heavy-duty trucks,
132 light-duty trucks and large passenger cars), gasoline vehicles (GV) (small cars and
133 motorcycles), and liquefied petroleum gas vehicles (LPGV) (bus and taxies). The
134 average traffic density during sampling was 1797 per hour with DV, GV and LPGV

proportion of 13.7 ± 2.7%, 59.8 ± 8.8% and 26.5 ± 7.9% respectively. More details of the vehicle counts and meteorological conditions are summarized in Table S1 of the Supplement.

2.2 Chemical analysis

The $PM_{2.5}$ mass concentrations were determined gravimetrically by weighing the quartz filters before and after sampling. The samples were conditioned in an electronic hygrothermostat for 24 h at 25 °C and 50% relative humidity (RH) before weighing. Then, samples were analyzed for OC/EC, WSOC, WSII, metal elements, organic compounds and stable carbon isotope. The experimental methods of the chemical analysis are available in the Supplement.

2.3 Calculation of emission factor

Average emission factor (*EF*) was calculated for each sampling period on the basis of the concentration difference between the exit and entrance of the tunnel by the following equation (Handler et al., 2008):

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

where *EF* is the emission factor of a species in unit of mg vehicle^{-1} km^{-1}, *N* is the number of vehicles passing through the tunnel, *L* is the distance between inlet and outlet sampling locations, C_{out} and C_{in} are the measured species concentration at the tunnel outlet and inlet, respectively, and *V* is the corresponding air volume calculated

156 from the cross-sectional area of the tunnel, the average wind speed, and the sampling
157 duration of each filter. The average concentrations of all measured species at the inlet
158 and outlet sampling locations and the corresponding emission factors in this study are
159 presented in Tables S2-4 of the Supplement.
160
161 **3. Results and discussion**
162 ***3.1 Characteristics of $PM_{2.5}$ emissions from vehicles in the PRD region***
163 *3.1.1 $PM_{2.5}$ mass, OC, EC, WSOC, WSII, metal elements*
164 The $PM_{2.5}$ mass emission factors ranged from 79.8 to 107 mg vehicle^{-1} km^{-1},
165 with an average of 92.4 ± 8.9 mg vehicle^{-1} km^{-1}. Average OC and EC emission factors
166 were 16.7±1.9 and 16.4±2.1 mg vehicle^{-1} km^{-1}, respectively, and they accounted for
167 19 ± 2% and 18 ± 2% of $PM_{2.5}$ mass emission. The ratio of OC to EC in the Zhujiang
168 Tunnel ranged from 0.77 to 1.35, with an average of 1.03. Previous studies have
169 shown that the OC/EC ratio is useful to separate gasoline engine emissions from
170 diesel emissions. Higher values (> 2) are associated with GV and LPGV exhaust, and
171 lower values (0.3 to ~0.9) associated with DV exhaust (Cadle et al., 1999; Cheng et
172 al., 2010; Gillies and Gertler, 2000). Therefore, the low OC/EC ratios in this study,
173 which are closer to that from DV exhaust, indicate that diesel vehicles played an
174 important role in the $PM_{2.5}$ emission although the proportion of DV was only 13.7%
175 during the sampling. Additionally, it should be noted that emissions of EC from heavy
176 duty trucks are expected to be relatively low under the low speed operating conditions

177 in the tunnel (Kweon et al., 2002). Therefore, the ratio could be lower at the actual
178 driving condition of vehicle fleet with a higher speed on the road. The concentration
179 of WSOC at the inlet was 6.21 μg m^{-3} (Table S2 of the Supplement) with a percentage
180 of 31.1% of OC, which is close to that of ambient air (Ding et al., 2008; Ho et al.,
181 2006). At the outlet of the tunnel, the concentration of WSOC was 8.00 μg m^{-3},
182 representing 17.9% of OC. The WSOC had been reported to contribute on average 20%
183 to OC in the exit of Marseille roadway tunnel (El Haddad et al., 2009), in which
184 background influence was included. The calculated emission factor of WSOC in this
185 study ranged from 0.5 to 2.8 mg $vehicle^{-1}$ km^{-1}, with an average of 1.31 mg $vehicle^{-1}$
186 km^{-1}, which consisted of 7.84% of OC. Such a WSOC fraction is considerably lower
187 than that previously measured for biomass burning particles (71%) (Mayol-Bracero et
188 al., 2002). However, it could influence the hygroscopicity of particles and the
189 formation of secondary aerosols (Ho et al., 2006; Rogge et al., 1993b; Weber et al.,
190 2007) and is worthy of more attention and in-depth research.
191 The sum of WSII comprised about 9.8% of the $PM_{2.5}$ emission, with emission
192 factors of 4.17, 0.104, 0.609, 2.88, 0.165, 0.177 and 0.953 mg $vehicle^{-1}$ km^{-1} for Cl^-,
193 NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+} and Ca^{2+}, respectively. The other WSII had a minor
194 contribution (< 0.1 mg $vehicle^{-1}$ km^{-1}). Totally 27 measured metal elements
195 contributed 15.2% to the $PM_{2.5}$ emission. Fe was the most abundant element, with an
196 emission factor of 3.91 mg $vehicle^{-1}$ km^{-1}, followed by Na 3.53 mg $vehicle^{-1}$ km^{-1}, Al
197 3.15 mg $vehicle^{-1}$ km^{-1}, Ca 1.93 mg $vehicle^{-1}$ km^{-1}, Mg 0.496 mg $vehicle^{-1}$ km^{-1}, and K

198 0.338 mg vehicle^{-1} km^{-1}, which accounted for 4.2%, 3.8%, 3.4%, 2.1%, 0.5%, and 0.4%
199 of $PM_{2.5}$ mass emission respectively. These six elements contributed 95.0% to the
200 total metal emission. Emission factors of other metals ranged from 0.0001 (Ag) to
201 0.25 (Ba) mg vehicle^{-1} km^{-1}, with a sum of 0.71 mg vehicle^{-1} km^{-1}. It is worth noting
202 that emission factors of elements including Na, K, Mg and Ca were significantly
203 higher than that of their corresponding water-soluble parts (Table S3 of the
204 Supplement). The differences can be attributed to the water-insoluble matter with
205 these metal elements, such as calcium and magnesium carbonates and Na-K-Mg
206 bearing aluminosilicate species (Pio et al., 2013).

207 $PM_{2.5}$ mass was also obtained by summing OM, EC, geological component, sea
208 salt, and major water soluble inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-). OC was multiplied
209 by 1.4 to estimate mass of OM (He et al., 2008). The geological component of 35 mg
210 vehicle^{-1} km^{-1} was estimated based on the Al emission data as present in Table S3 of
211 the Supplement. A typical road dust Al composition is 9% on average (Tiittanen et al.,
212 1999). Sea salt of 9 mg vehicle^{-1} km^{-1} was estimated by Na assuming sea salt contains
213 32% of Na. Thus, the average $PM_{2.5}$ reconstructed mass was 91.8% of the gravimetric
214 value. This discrepancy can be attributed to the uncertainties in the weighing process,
215 the estimation methods and uncalculated components.

216

217 *3.1.2 Organic compounds*

218 The average emission factors and abbreviated names of 67 individual organic

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

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

240 factors for other compounds ranged from 0.006 (acenaphthene) to 0.89 (pyrene) μg
241 vehicle^{-1} km^{-1} (Table S4 of the Supplement). Pyrene was the most abundant
242 compound, followed by chrysene (CHR), benzo[ghi]perylene (BghiP) and
243 benz[a]anthracene (BaA), which is different from biomass burning and coal
244 combustion (Huang et al., 2014; Shen et al., 2012). PAHs diagnostic ratios have been
245 used as a tool for identifying pollution emission sources including ANT/(ANT+PHE),
246 FLA/(FLA+PYR), BaA/(BaA+CHR), BbF/(BbF+BkF), IcdP/(IcdP+BghiP) and
247 BaP/(BaP+BghiP) (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002; Zhang et
248 al., 2005). We summarized PAHs ratios mentioned above in Fig. 2 for three
249 combustion sources including vehicle emission, biomass burning and coal combustion.
250 On the whole, the six ratios in this study are similar to the other tunnel experiments,
251 though environmental conditions of tunnels are different to some extent. It is also
252 suggested that the ratio of FLA/(FLA+PYR) and IcdP/(IcdP+BghiP) might be more
253 suitable to distinguish vehicle emission from biomass burning and coal combustion.
254 Hopanes and steranes are known molecular markers of aerosol emissions from
255 fossil fuel utilization (Simoneit, 1985). Rogge et al. (1993a) and Schauer et al. (1996)
256 had shown that these petroleum biomarkers can be used to trace motor vehicle
257 exhaust contributions to airborne PM in southern California atmosphere. Fourteen
258 major hopanes homologues with emission factors ranging from 0.46 ~ 9.14 μg
259 vehicle^{-1} km^{-1} and twelve steranes homologues ranging from 0.31 ~ 0.97 μg vehicle^{-1}
260 km^{-1} were identified in this study. 17α(H),21β(H)-hopane (HP30) was the most

abundant component with the emission factor of 9.14 μg vehicle^{-1} km^{-1}. The emission factor of total hopanes was 32.0 μg vehicle^{-1} km^{-1}. Emissions of the S hopanes for the extended 17α(H),21β(H)-hopane homologues > C31 were always higher than those of the corresponding R pairs. All these characteristics of hopanes in the Zhujiang Tunnel are consistent with those in gasoline and diesel exhausts (Rogge et al., 1993a; Simoneit, 1985) and in other tunnel studies (see Fig. S1 of the Supplement). Emission factors of individual sterane ranged from 0.31 to 0.97 ng vehicle^{-1} km^{-1}, and the sum of their emission factors was 7.58 μg vehicle^{-1} km^{-1}. The most abundant homologue was C29αββ-stigmastane (20R) (29αββR), followed by 29αααS and 29αββS.

3.1.3 Stable carbon isotope

Stable carbon isotope analysis of vehicle emissions in Zhujiang Tunnel yielded $\delta^{13}C$ values ranging from -25.5 to -24.7‰ with an average value of -25.0 ± 0.2‰, and is comparable to previously reported ranges of -29 to -24.6‰ (Table 1) for vehicular fuel emission. Generally, the variation in $\delta^{13}C_{Fuel}$ could affect the $\delta^{13}C$ of hydrocarbons (Keppler et al., 2004; Yamada et al., 2009). In the PRD region, the $\delta^{13}C$ value of gasoline was on average -28.6 ± 0.6‰, and the $\delta^{13}C$ value of diesel was –27.8 ± 0.2‰, and small variation of fuel $\delta^{13}C$ was observed (Hu et al., 2014). We calculated the isotopic differences between $\delta^{13}C_{PM2.5}$ and $\delta^{13}C_{Fuel}$, which represents the apparent isotopic fractionation occurring during fuel burning. It expressed as $\Delta^{13}C$ (‰), and is defined by the following equation (Yamada et al., 2009).

282 $$\Delta^{13}C_{PM2.5-Fuel} = (\frac{\delta^{13}C_{PM2.5} + 1000}{\delta^{13}C_{Fuel} + 1000} - 1) \times 1000$$

283 In this study, the value of $\Delta^{13}C_{PM2.5\text{-}Fule}$ was from 2.7 to 3.5 ‰, with an average
284 of 3.2 ‰, indicating an isotopic fractionation occurred during fuel combustion.
285 Comparing the stable isotopic carbon value of vehicular fuel emission with other
286 particulate emission sources (see Table 1), it is found that different emission sources
287 showed different stable carbon isotopic composition. For total carbon in $PM_{2.5}$ sample,
288 $\delta^{13}C$ (‰) of coal and fuel oil combustion are -23.9‰ and -26.0‰ respectively, while
289 that of vehicle emission is -25.9~-25.0‰. Obviously, the $\delta^{13}C$ (‰) of vehicle
290 emission is not significantly different from that of coal and fuel oil combustion.
291 However, they are obviously different from other sources, like dust particle
292 (-21~-18.4‰), C3 plant (-19.3~-13‰), and C4 plant (-34.7~-27‰). Therefore, $\delta^{13}C$
293 might be used to distinguish the fossil fuel combustion from the other sources.
294
295 ***3.2 Comparison with previous studies conducted in the same tunnel***
296 To investigate the variation of chemical emission characteristics from vehicles in
297 the PRD region over the past decade, we compared the chemical emission
298 characteristics of this study with that of previous study (He et al., 2008) for the same
299 tunnel in 2004 (see Figs 3 and 4). Fig. 3 shows that $PM_{2.5}$ mass, OC, EC decreased
300 significantly from 2004 to 2013. The reason can be partly attributed to the
301 implementation of pollution control measures for Chinese vehicle emission. During
302 this 9-year period, vehicle emission standard have raised two levels (from China II in

303 2004 to China IV in 2013) (Table 2). Additionally, comparing the fleet composition
304 of 2013 with 2004 in Zhujiang Tunnel, we found that the proportion of DV and GV
305 decreased while that of LPGV increased. LPG is a type of clean energy, and LPGV is
306 known to emit much less PM mass than GV and DV, while DV emits the most PM
307 mass (Allen et al., 2001; Myung et al., 2014; Yang et al., 2007). LPG could be
308 combusted more completely than gasoline and diesel. Changes mentioned above
309 contributed greatly to the decrease of emission factors of OC and EC (31.3% and
310 66.9%) and $PM_{2.5}$ mass (16.0%) from 2004 to 2013. However, the emissions of $PM_{2.5}$
311 mass, OC and EC are still quite higher than those measured in other countries (see
312 Table S5 of the Supplement). The implication of these high emission levels is that
313 both the fuel quality and engine technologies in the PRD region need to be further
314 improved.

315 It is also found from Fig. 3 that emission factors of NO_3^-, SO_4^{2-} and NH_4^+
316 decreased from 2004 to 2013. Improvement of fuel quality resulted in decreasing of
317 sulfate emission factor from 3.18 to 0.61 mg vehicle^{-1} km^{-1}, since the amount of sulfur
318 in fuel is slashed by 81.5~ 95 % in China IV (2013) when compared that in China II
319 (2004) (Table 3). The emission levels of nitrate and ammonium were about one-tenth
320 of those observed in 2004, possibly because NOx emission standard is tightened from
321 2004 to 2013 (Table 2) leading to the less production of ammonium nitrate. Emission
322 factor of chloride is quite higher than that obtained from Zhujiang Tunnel in 2004 and
323 other tunnels. Chloride was found up to 74 mg vehicle^{-1} km^{-1} in PM_{10} in the Howell

Tunnel, due to the application of salt to melt ice on roadways in the winter (Lough et al., 2005). However, it is not applicable in Guangzhou City. The good correlation between Cl^- and Na^+ (r^2=0.992) indicates the re-suspension of sea salt particles combined with vehicle emission PM might be a major source (He et al., 2008).

Emission factors of most of the metal elements increased in Zhujiang Tunnel from 2004 to 2013 except Cd and Pb. Na emission increased 3.18 mg $vehicle^{-1}$ km^{-1} in 2013 than in 2004. Na correlated weakly with Cl^- (r^2=0.374) and Na^+ (r^2=0.429). This indicates that Na emission had other sources and it was not only from the re-suspension of sea salt particles. The other four most abundant elements including Fe, Ca, Mg, K increased by one to three times, probably because of resuspended road dust. However, the wind speed in 2013 was found to be higher but not significantly than that in 2004 (3.8 m s^{-1} in 2013 versus 3.0 m s^{-1} in 2004). This minor difference in wind speed could not account for the large increase. Furthermore, examination of the number of vehicles per hour in 2013 and 2004 suggests that there were fewer vehicles per hour in 2013. Therefore, a more plausible explanation is that there was a lot more dust on the road in 2013. Other sources would cause the increased emissions of these elements, such as oil additive (Mg, Ca, Cu, Zn. (Cadle et al., 1997)) and the wear of engines (Fe) (Cadle et al., 1997; Garg et al., 2000), brakes and tires (Al, Fe,Cu, Mn, Cd, Ni, Pb and Zn. (Garg et al., 2000; Pio et al., 2013)). Additionally, emissions of Zn, Cu, Mn, Cr, Ni, V, As, Co, U, and Tl increased by 0.5 to 4.5 times. Although the sum of these elements did not exceed 0.5% of $PM_{2.5}$ mass, they are important for health

345 effects. Lower emission factor of Pb (0.01±0.0007 mg vehicle^{-1} km^{-1}) in 2013 than in
346 2004, could be a result of the phase out of leaded gasoline across China in the late
347 1990s.

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

366 PAHs decreased by 67.6% ~ 93.4%. BaP equivalents (BaPeq) emission factors
367 decreased by 88.1% from 2004 to 2013 (Table S6 of the Supplement). This could be
368 attributed to the variation of fleet composition between 2004 and 2013. PAHs emitted
369 from LPGV are about one-third of that from GV (Yang et al., 2007), while DV emit
370 more PAHs than GV (Phuleria et al., 2006). Therefore, higher proportion of LPGV
371 and lower proportion of DV resulted in the lower emission factor of PAHs in 2013
372 than that in 2004. Emission factors of hopanes also decreased from 2004 to 2013, the
373 percentage of decrease ranged from 56.2% to 68.7%. However, the distributions of
374 hopane series derived from different tunnel studies were very similar (see Fig. S2 of
375 the Supplement). This suggests that the hopane emission characteristics might be
376 independent of the fleet composition. This is a reasonable result given that hopanes
377 originate from the lubricating oil used in DV, GV and LPGV rather than from the fuel
378 (He et al., 2008; Phuleria et al., 2006). Owing to more units in heavy-duty vehicle
379 need lubrication, emission factors of hopanes attributable to heavy-duty vehicle were
380 higher than that to light-duty vehicle (Phuleria et al., 2006). Reduction of the
381 proportion of heavy-duty vehicle (bus, heavy-duty truck, large passenger cars)
382 proportion in fleet composition in 2013 (11.3%) compared that in 2004 (20%) might
383 be the reason that emission factors of hopanes decreased.
384
385 ***3.3 Implication for vehicle emission control policy***
386 Vehicle emission control strategies and policies adopted by Guangdong Province

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

408 year. As shown in Fig. 5a, the total vehicle population increased by 49.1% from 2004
409 to 2013. Total emission of vehicle exhaust of $PM_{2.5}$ mass (calculated as emission
410 factors multiply by annual average driving distance per car and vehicle population
411 (Wu et al., 2012)) increased by 25.2% from 2004 to 2013 (Fig. 5b). Consequently, it
412 is demonstrated that more stringent emission standards and higher quality of fuel or
413 more utilization of clean fuels will be necessary to offset the impacts on the growth in
414 vehicle population and to improve air quality in the PRD region. Additionally, owing
415 to no mandatory national standards to limit metal content from vehicle emission, the
416 emission of majority of metals increased from 2004 to 2013 (Fig. 3 and 5b). In China,
417 heavy metals, including As, Cr, Cu, Ni and Tl, had been listed as key substances that
418 should be preferentially monitored in the atmospheric environment (SEPA, 2003) and
419 thus the increases of metal elements should raise the awareness of the government due
420 to their health concern.
421
422 **4. Conclusions**
423 $PM_{2.5}$ samples were collected between August 10 and 14, 2013 in Guangzhou
424 Zhujiang Tunnel to acquire a comprehensive snapshot of the chemical characteristics
425 of vehicle emission. The average emission factors of $PM_{2.5}$ mass, EC, OC, WSOC,
426 WSII, metal elements, organic compounds and stable carbon isotope were measured.
427 Stable carbon isotope $\delta^{13}C$ value indicates an isotopic fractionation of 3.2‰ occurred
428 during fuel combustion. Compared with a previous study in Zhujiang Tunnel in year

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

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

Emission sources and Sampling site	Particle types	$\delta^{13}C$ 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)

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

664 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

665 [a] Year of implementation; [b] for light duty vehicle; [c] for compression ignition and gas fuelled positive ignition

666 engines of vehicles.

667 **Table 3.** Vehicle fuel standard and limit for sulfur content (mg kg^{-1}) implemented in

668 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

669 [a] Year of implementation; [b] unit: mg m^{-3}

Figure captions:

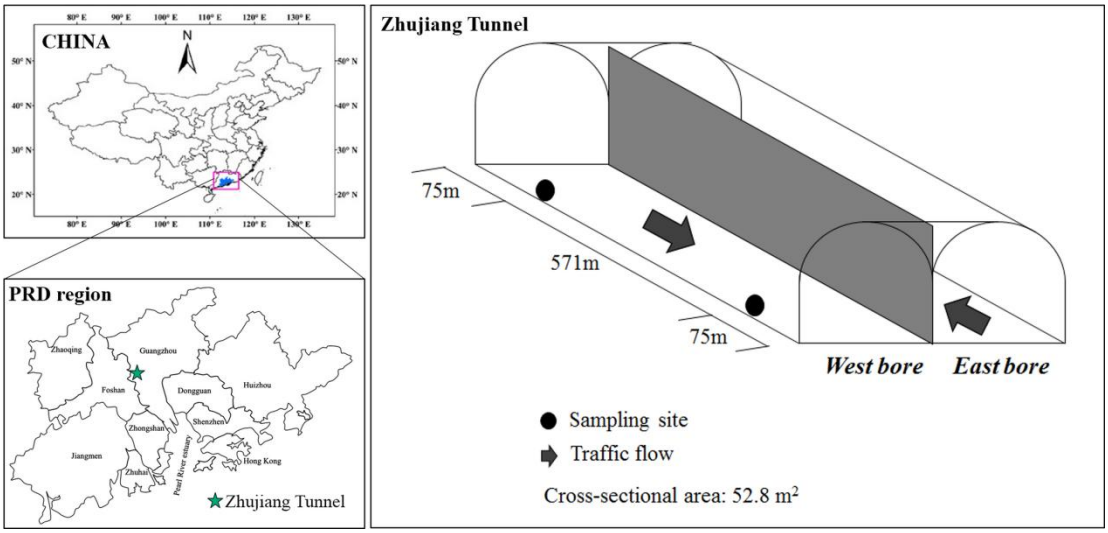
Fig. 1. Sampling schematic diagram of the Zhujiang Tunnel.

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

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

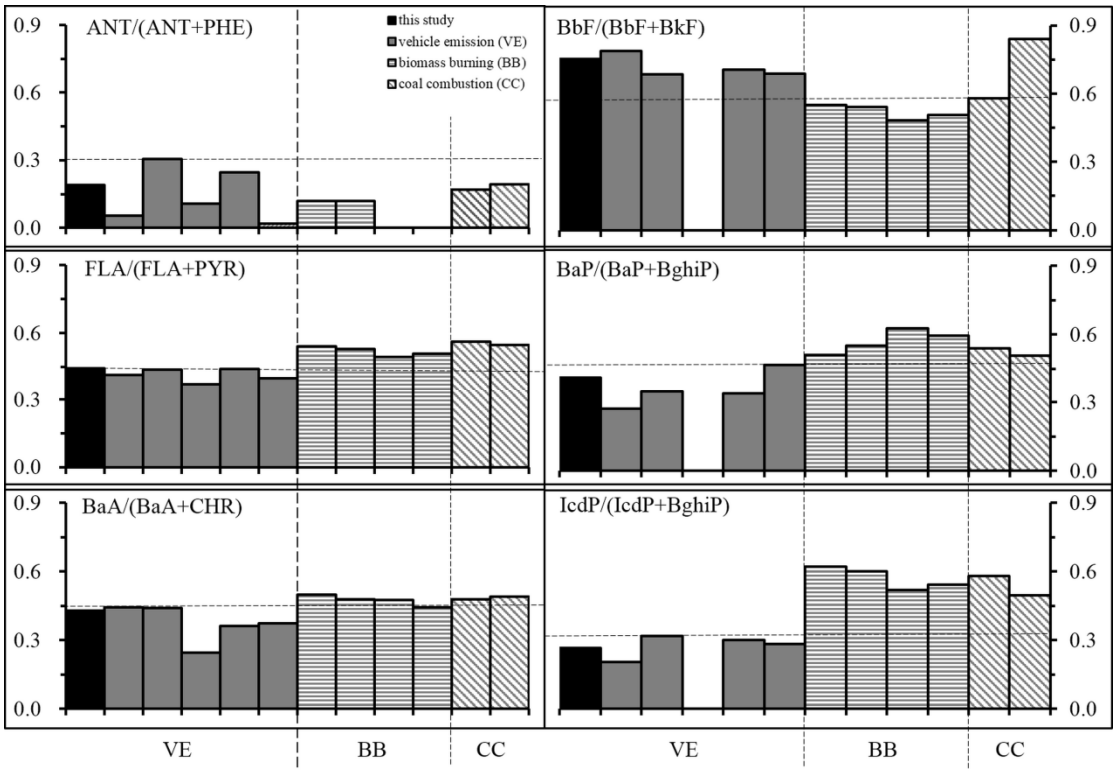
Fig. 4. Comparison of organic compounds emissions in the Zhujiang Tunnel sampling in 2004 and 2013.

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


CHINA
N
80° E
90° E
100° E
110° E
120° E
130° E
50° N
40° N
30° N
20° N
PRD region
Zhaoqing
Guangzhou
Foshan
Dongguan
Huizhou
Zhongshan
Shenzhen
Jiangmen
Zhuhai
Hong Kong
Pearl River estuary
Zhujiang Tunnel
Zhujiang Tunnel
75m
571m
75m
West bore
East bore
Sampling site
Traffic flow
Cross-sectional area: 52.8 m²

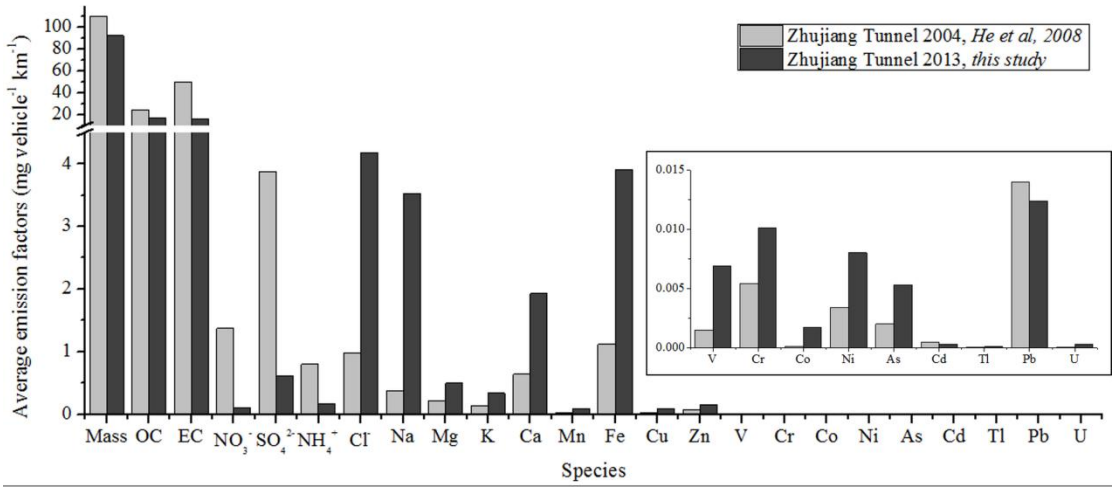
691 Fig. 1

692


ANT/(ANT+PHE)
this study
vehicle emission (VE)
biomass burning (BB)
coal combustion (CC)
BbF/(BbF+BkF)
FLA/(FLA+PYR)
BaP/(BaP+BghiP)
BaA/(BaA+CHR)
IcdP/(IcdP+BghiP)
0.0
0.3
0.6
0.9
VE
BB
CC

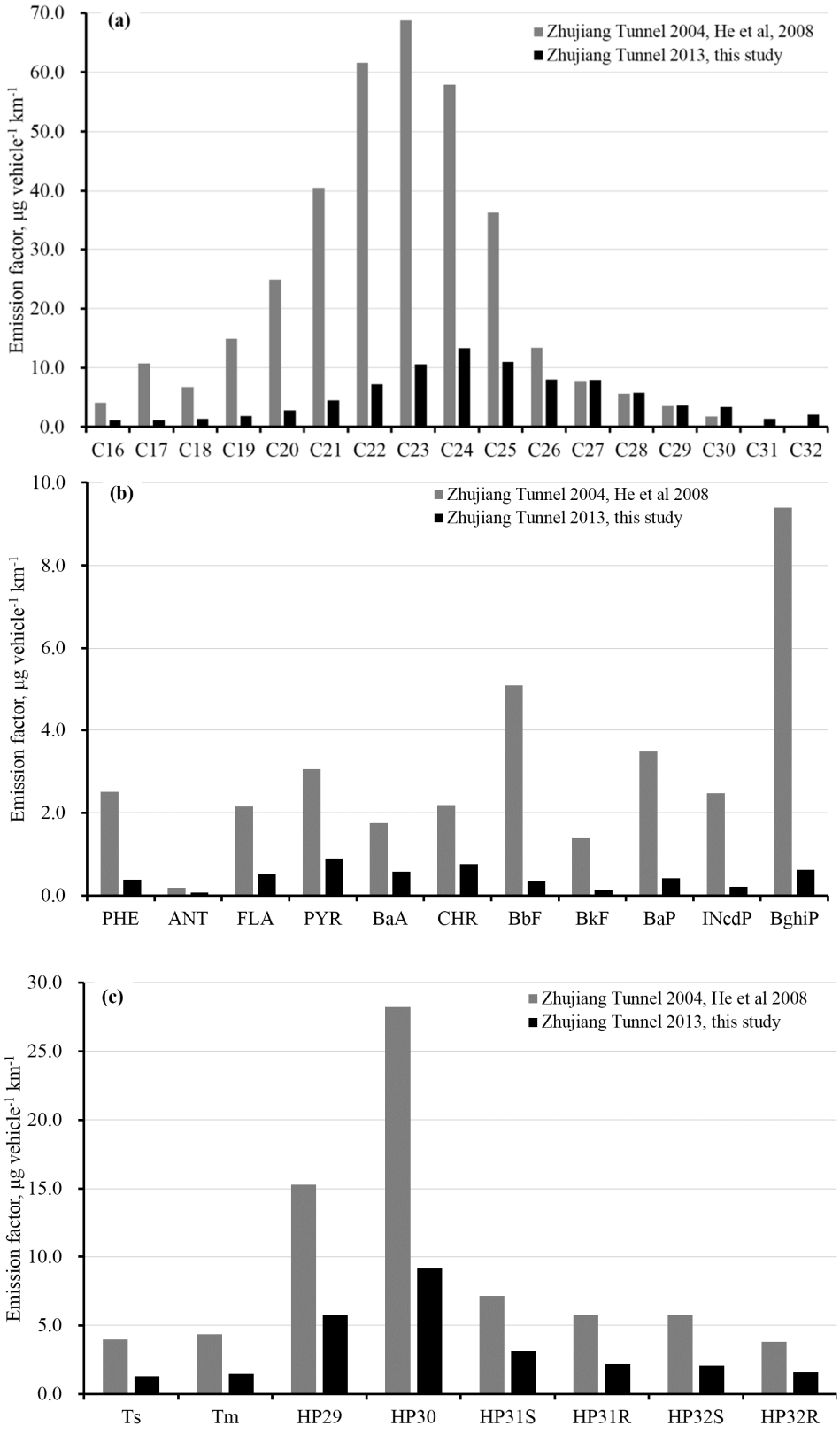
693 Fig. 2

694

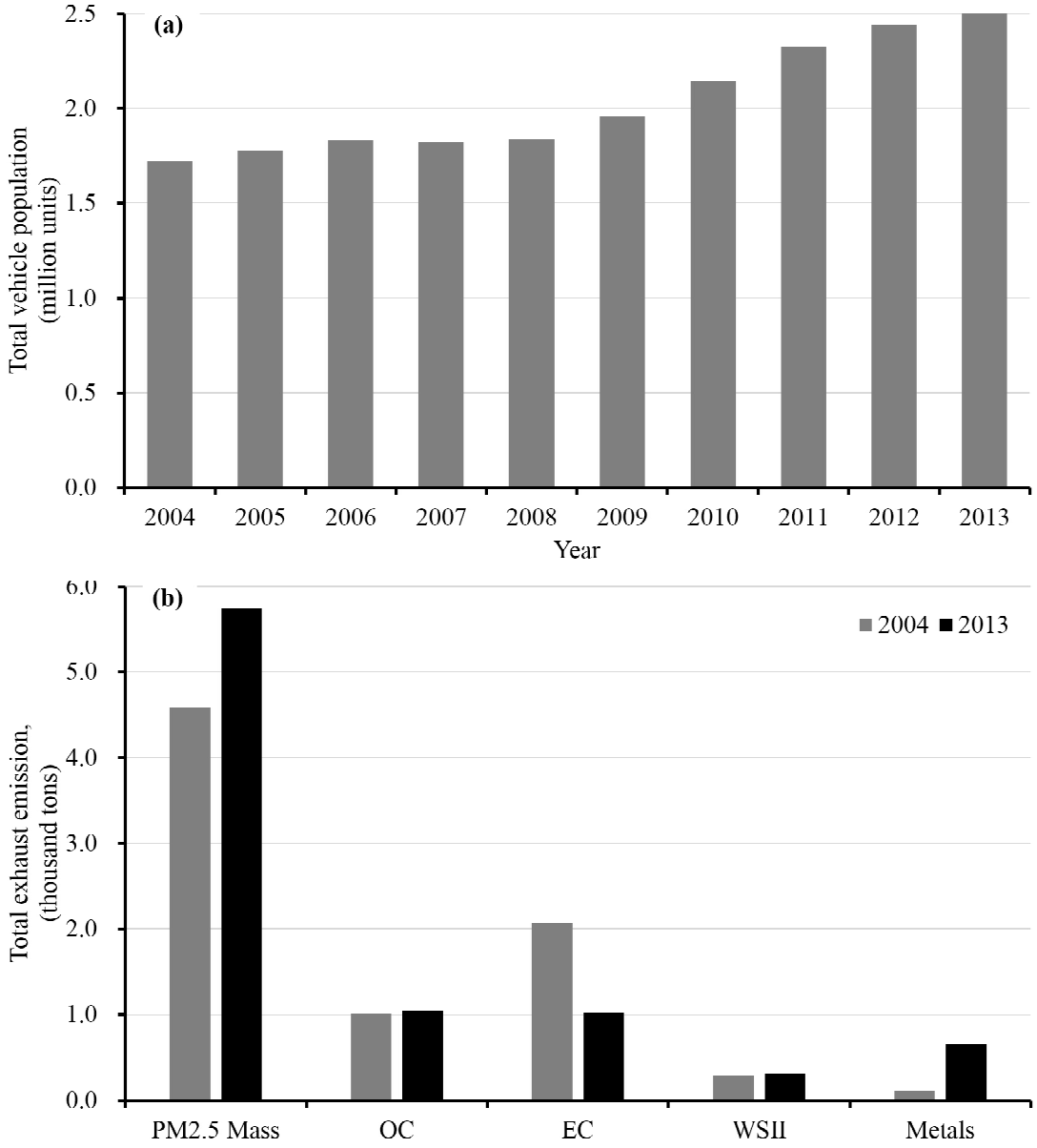

Zhujiang Tunnel 2004, He et al, 2008
Zhujiang Tunnel 2013, this study
Average emission factors (mg vehicle-1 km-1)
Species
Mass OC EC NO3- SO4 2- NH4+ Cl- Na Mg K Ca Mn Fe Cu Zn V Cr Co Ni As Cd Tl Pb U
V Cr Co Ni As Cd Tl Pb U

695 Fig. 3

696


(a)
Zhujiang Tunnel 2004, He et al, 2008
Zhujiang Tunnel 2013, this study
Emission factor, μg vehicle-1 km-1
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
C16 C17 C18 C19 C20 C21 C22 C23 C24 C25 C26 C27 C28 C29 C30 C31 C32
(b)
Zhujiang Tunnel 2004, He et al 2008
Zhujiang Tunnel 2013, this study
Emission factor, μg vehicle-1 km-1
10.0
8.0
6.0
4.0
2.0
0.0
PHE ANT FLA PYR BaA CHR BbF BkF BaP INcdP BghiP
(c)
Zhujiang Tunnel 2004, He et al 2008
Zhujiang Tunnel 2013, this study
Emission factor, μg vehicle-1 km-1
30.0
25.0
20.0
15.0
10.0
5.0
0.0
Ts Tm HP29 HP30 HP31S HP31R HP32S HP32R

697 Fig. 4


(a)
Total vehicle population (million units)
2.5
2.0
1.5
1.0
0.5
0.0
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
Year
(b)
2004
2013
Total exhaust emission, (thousand tons)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PM2.5 Mass
OC
EC
WSII
Metals

698 Fig. 5

699