



# Chemical and stable carbon isotopic composition of PM<sub>2.5</sub> from on-road vehicle emissions in the PRD region and implications for vehicle emission control policy

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**Abstract.** Vehicle emissions are a major source of urban air pollution. In recent decade, the Chinese government has introduced a range of policies to reduce vehicle emissions. In order to understand the chemical characteristics of PM<sub>2.5</sub> from on-road vehicle emissions in the Pearl River Delta (PRD) region and to evaluate the effectiveness of control policies on vehicle emissions, the emission factors of PM<sub>2.5</sub> 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<sub>2.5</sub> mass, OC, EC and WSOC were 92.4, 16.7, 16.4 and 1.31 mg vehicle<sup>-1</sup> km<sup>-1</sup> respectively. Emission factors of WSII were 0.016 (F<sup>-</sup>) ~ 4.17 (Cl<sup>-</sup>) mg vehicle<sup>-1</sup> km<sup>-1</sup>, contributing about 9.8% to the PM<sub>2.5</sub> emissions. The sum of 27 measured metal elements accounted for 15.2% of PM<sub>2.5</sub> emissions. Fe was the most abundant metal element, with an emission factor of 3.91 mg vehicle<sup>-1</sup> km<sup>-1</sup>. Emission factors of organic compounds including *n*-alkanes, polycyclic aromatic hydrocarbons, hopanes and steranes were 91.9, 5.02, 32.0 and 7.59 μg vehicle<sup>-1</sup> km<sup>-1</sup>, respectively. Stable carbon isotopic composition δ<sup>13</sup>C value was -25.0‰ on average. An isotopic fractionation of 3.2‰ was found during fuel combustion. Compared to a previous study in Zhujiang tunnel in 2004, emission factors of PM<sub>2.5</sub> mass, EC, OC, WSII except Cl<sup>-</sup> 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 emissions, which should be a concern of the government. A snapshot of the 2013 characteristic emissions of PM<sub>2.5</sub> and its constituents from the on-road vehicular fleet in the PRD region retrieved from our study would be helpful for the assessment of past and future implementations of vehicle emission control policy.

## 1 Introduction

Vehicle emissions are a major source of urban air pollution and account 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 emissions have been our concern during the last decades. Numerous studies have been conducted to characterize vehicular particulate matter (PM) emissions 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 emissions in China were studied by tunnel experiments, dynamometer tests and 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 emissions from vehicles varied over regions and time.

The Pearl River Delta (PRD) region, located on the southern coast of China, has experienced serious atmospheric pollution with its rapid urbanization and industrialization in the last few decades. Vehicle emissions account for approximately 25–30% of total fine PM in the PRD region ([http://epaper.southcn.com/nfdaily/html/2014-01/03/content\\_7261687.htm](http://epaper.southcn.com/nfdaily/html/2014-01/03/content_7261687.htm)). Peer-reviewed papers have reported emission factors and chemical characteristic of PM<sub>2.5</sub> from vehicle emissions in the PRD region by means of tunnel studies in the Zhujiang (Guangzhou) and Wutong (Shenzhen) tunnels (He et al., 2006, 2008; X. F. Huang et al., 2006). However, the sampling in these studies was conducted in 2004. The Environmental Protection Agency of Guangdong revised the motor-vehicle-exhaust-pollution prevention and control regulations of Guangdong in 2008 and released the “PRD Regional Air Quality Management Plan” and “A Clean Air Plan” in 2010 to improve the relevant air quality through policies and measures. The emission standards for newly registered vehicles were tightened to China IV standards and better-quality gasoline and diesel were supplied in 2013. Therefore, the characteristics of PM emissions from vehicles in the PRD region might have changed throughout these years.

Tunnel experiments and chassis dynamometer tests were widely used to measure various pollutants emitted from vehicles (He et al., 2006; Heeb et al., 2003). However, dynamometer test is limited because it cannot account for vehicle fleet composition and emission characteristics related to break and tire wear and resuspension of road dust (Thorpe and Harrison, 2008). Tunnel studies have been demonstrated to be a suitable setup to measure PM emissions from on-road mixed fleets (Chiang and Huang, 2009; Laschober et al., 2004; Pio et al., 2013).

This study was carried out in a roadway tunnel located in the PRD region. We report here the emission factors of PM<sub>2.5</sub> mass, organic carbon (OC), elemental carbon (EC), water-soluble inorganic ions (WSII), metal elements, water-soluble organic carbon (WSOC), organic compounds and stable carbon isotopic composition. WSOC has the potential to modify the hygroscopicity of particles, PM size and cloud condensation nuclei activities (Shulman et al., 1996); however, it is often ignored in previous studies owing to the hydrophobic nature of the organic aerosol from primary vehicle emissions. Stable carbon isotope ( $\delta^{13}\text{C}$ ) is very useful for tracing sources (Lopez-Veneroni, 2009; Widory, 2006), and it was also less reported for vehicular exhaust emissions (Ancelet et al., 2011; Widory, 2006). The objectives of this study are (1) to obtain comprehensive information on the chemical and stable carbon isotopic composition of PM<sub>2.5</sub> emissions from on-road vehicles in the PRD region; (2) to compare our results with the previous study conducted in the same tunnel in 2004; (3) to evaluate the effectiveness of the implementation

of vehicle emission control policies from 2004 to 2013 in the PRD region. Although the fleet composition in this tunnel was probably different from the vehicle composition in the PRD region, it does not affect the conclusions in this paper.

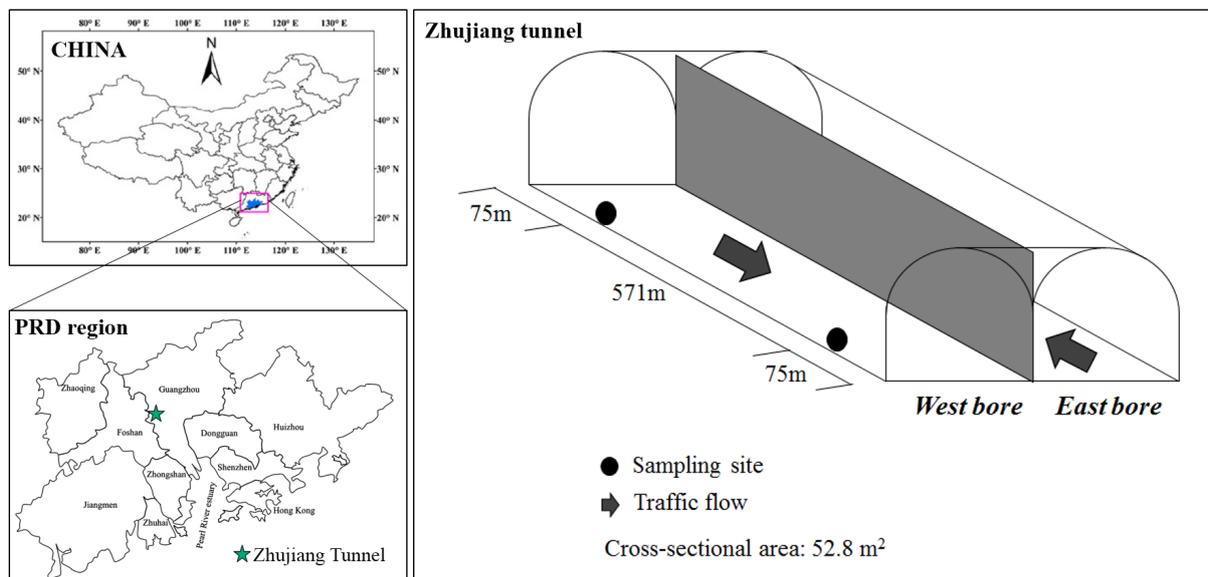
## 2 Experimental

### 2.1 Tunnel sampling

PM<sub>2.5</sub> samples were collected from 10 to 14 August 2013 from the roadway tunnel (Zhujiang tunnel) located in Guangzhou, China. It has two bores, each of which has three lanes with traffic in the same direction, as shown in Fig. 1. Two high-volume PM<sub>2.5</sub> samplers (GUV-15HBL1, Thermo, USA) were placed at a distance of 75 m from the entrance and 75 m from the exit. The vehicle speed in the Zhujiang tunnel was 18 to 45 km h<sup>-1</sup>, with an average vehicle speed of 33.4 km h<sup>-1</sup> during the sampling. The PM samples were collected at about 1.13 m<sup>3</sup> min<sup>-1</sup> through the quartz fiber filters (QFFs, 20.3 cm × 25.4 cm, Whatman). Other devices such as diffusion denuders and foam plugs were not used due to the difficulties in applying these devices. Consequently, volatilization losses or adsorption artifacts may occur on the filter for semi-volatile organic compounds, especially for the low molecular weight compounds due to their high volatility (Kavouras et al., 1999). However, the calculation of emission factors was based on the concentration differences between the exit and entrance of the tunnel; thus, the potential losses or adsorption artifacts of semi-volatile organic compounds would be partly deducted. Field blank samples were also collected by loading filters into the samplers but without pulling air through. The ventilation system of the tunnel was turned off during the sampling period; thus, the dispersion of air pollutants in the tunnel was mainly due to the piston effect arising from the traffic flow. The sampled filters were wrapped with annealed aluminum foil and stored in a refrigerator at -40 °C until analysis. The meteorological parameters were synchronously recorded. A video camera was placed at the exit to record the passing vehicles during the sampling periods. The videotapes were then used to determine the vehicle counts and to classify the vehicles into three categories, namely, diesel vehicles (DV) (heavy-duty trucks, light-duty trucks and large passenger cars), gasoline vehicles (GV) (small cars and motorcycles) and liquefied petroleum gas vehicles (LPGV) (buses and taxis). The average traffic density during sampling was 1797 per hour with DV, GV and LPGV proportions 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 in the Supplement.

### 2.2 Chemical analysis

The PM<sub>2.5</sub> mass concentrations were determined gravimetrically by weighing the quartz filters before and after sam-



**Figure 1.** Sampling schematic diagram of the Zhujiang tunnel.

pling. The samples were conditioned in an electronic hygrothermostat for 24 h at 25 °C and 50 % relative humidity 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 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):

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

where EF is the emission factor of a species in unit of  $\text{mg vehicle}^{-1} \text{ km}^{-1}$  or  $\mu\text{g vehicle}^{-1} \text{ km}^{-1}$ ,  $N$  is the number of vehicles passing through the tunnel,  $L$  is the distance between inlet and outlet sampling locations,  $C_{\text{out}}$  and  $C_{\text{in}}$  are the measured species concentration at the tunnel outlet and inlet, respectively, and  $V$  is the corresponding air volume calculated from the cross-sectional area of the tunnel, the average wind speed and the sampling duration of each filter. The average concentrations of all measured species at the inlet and outlet sampling locations and the corresponding emission factors in this study are presented in Tables S2–4.

## 3 Results and discussion

### 3.1 Characteristics of PM<sub>2.5</sub> emissions from vehicles in the PRD region

#### 3.1.1 PM<sub>2.5</sub> mass, OC, EC, WSOC, WSII, metal elements

The PM<sub>2.5</sub> mass emission factors ranged from 79.8 to 107  $\text{mg vehicle}^{-1} \text{ km}^{-1}$ , with an average of  $92.4 \pm 8.9 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ . Average OC and EC emission factors were  $16.7 \pm 1.9$  and  $16.4 \pm 2.1 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ , respectively, and they accounted for  $18.1 \pm 2.1$  and  $17.7 \pm 2.2$  % of PM<sub>2.5</sub> mass emissions. The ratio of OC to EC in the Zhujiang tunnel ranged from 0.77 to 1.35, with an average of 1.03. Previous studies have shown that the OC/EC ratio is useful to separate gasoline engine emissions from diesel emissions. Higher values (>2) are associated with GV and LPGV exhaust, and lower values (0.3 to ~0.9) are associated with DV exhaust (Cadle et al., 1999; Cheng et al., 2010; Gillies and Gertler, 2000). Therefore, the low OC/EC ratios in this study, which are closer to that from DV exhaust, indicate that diesel vehicles played an important role in the PM<sub>2.5</sub> emissions although the proportion of DV was only 13.7 % during the sampling. Additionally, it should be noted that emissions of EC from heavy-duty trucks are expected to be relatively low under the low-speed operating conditions in the tunnel (Kweon et al., 2002). Therefore, the ratio could be lower at the actual driving condition of vehicle fleet with a higher speed on the road. The concentration of WSOC at the inlet was  $6.21 \mu\text{g m}^{-3}$  (Table S2) with a percentage of 31.1 % of OC, which is close to that of ambient air (Ding

et al., 2008; Ho et al., 2006). At the outlet of the tunnel, the concentration of WSOC was  $8.00 \mu\text{g m}^{-3}$ , representing 17.9 % of OC. The WSOC had been reported to contribute on average 20 % to OC in the exit of Marseille roadway tunnel (El Haddad et al., 2009), in which background influence was included. The calculated emission factor of WSOC in this study ranged from 0.5 to  $2.8 \text{ mg vehicle}^{-1} \text{ km}^{-1}$  with an average of  $1.31 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ , which represents 7.84 % of that of OC. Such a WSOC fraction is considerably lower than that previously measured for biomass burning particles (71 %) (Mayol-Bracero et al., 2002). However, it could influence the hygroscopicity of particles and the formation of secondary aerosols (Ho et al., 2006; Rogge et al., 1993b; Weber et al., 2007) and is worthy of more attention and in-depth research.

The sum of WSII comprised about 9.8 % of the PM<sub>2.5</sub> emissions, with emission 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  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , respectively. The other WSII had a minor contribution ( $< 0.1 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ ). In total, 27 measured metal elements contributed 15.2 % to the PM<sub>2.5</sub> emissions. Fe was the most abundant element, with an 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  $3.15 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ , Ca  $1.93 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ , Mg  $0.496 \text{ mg vehicle}^{-1} \text{ km}^{-1}$  and K  $0.338 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ , which accounted for 4.2, 3.8, 3.4, 2.1, 0.5 and 0.4 % of PM<sub>2.5</sub> mass emissions, respectively. These six elements contributed 95.0 % to the total metal emissions. Emission factors of other metals ranged from 0.0001 (Ag) to 0.25 (Ba)  $\text{mg vehicle}^{-1} \text{ km}^{-1}$ , with a sum of  $0.71 \text{ mg vehicle}^{-1} \text{ km}^{-1}$ . It is worth noting that emission factors of elements Na, K, Mg and Ca were significantly higher than those of their corresponding water-soluble parts (Table S3). The differences can be attributed to the water-insoluble matter carrying these metal elements, such as calcium and magnesium carbonates and Na-, K- and Mg-bearing aluminosilicate species (Pio et al., 2013).

PM<sub>2.5</sub> mass was also obtained by summing OM, EC, geological component, sea salt and major water soluble inorganic ions ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ). OC was multiplied by 1.4 to estimate mass of OM (He et al., 2008). The geological component of  $35 \text{ mg vehicle}^{-1} \text{ km}^{-1}$  was estimated based on the Al emission data as presented in Table S3. A typical road dust Al composition is 9 % on average (Tiittanen et al., 1999). Sea salt of  $9 \text{ mg vehicle}^{-1} \text{ km}^{-1}$  was estimated by Na, assuming sea salt contains 32 % of Na. Thus, the average PM<sub>2.5</sub> reconstructed mass was 91.8 % of the gravimetric value. This discrepancy can be attributed to the uncertainties in the weighing process, the estimation methods and uncalculated components.

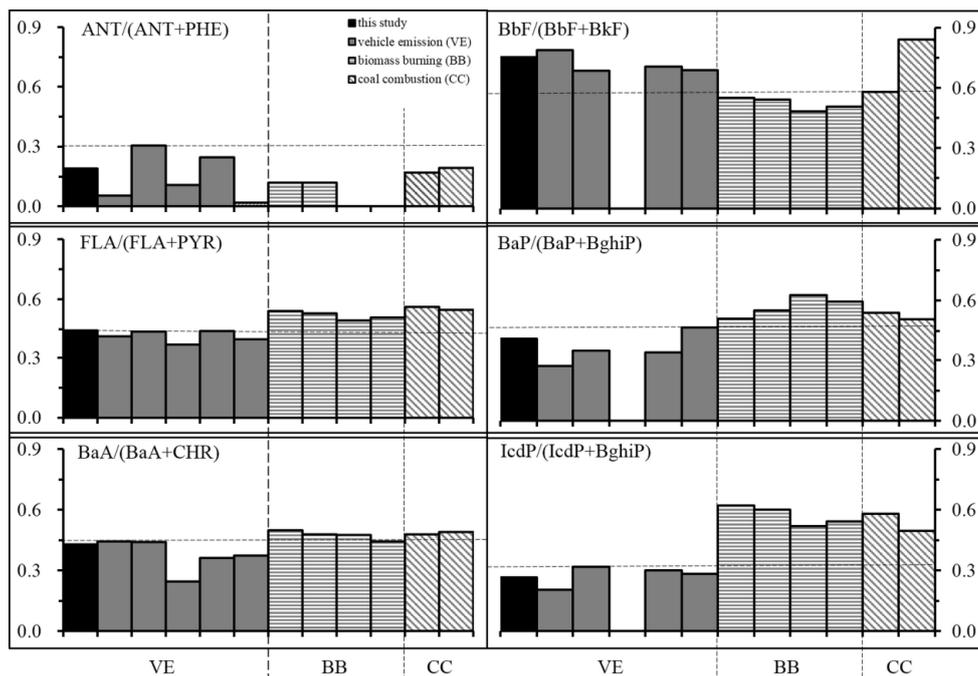
### 3.1.2 Organic compounds

The average emission factors and abbreviated names of 67 individual organic compounds identified in the Zhujiang tun-

nel, including *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes are listed in Table S4. These organic compounds accounted for 0.59 % of the OM and 0.11 % of the PM<sub>2.5</sub> mass emissions. The distributions of organic molecular markers associated with PM<sub>2.5</sub> are known to be source indicative despite 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 (1984, 1985). The emission factors of individual *n*-alkanes were in the range of 0.22 (C13) ~ 13.3 (C24)  $\mu\text{g vehicle}^{-1} \text{ km}^{-1}$  (Table S4).

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. In total, 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  $5.54 \mu\text{g vehicle}^{-1} \text{ km}^{-1}$  in this study. The emission factor of benzo[a]pyrene (BaP), which is often used as an indicator of PAHs and regarded by the World Health Organization as a good index for whole PAH carcinogenicity, was in the range of 0.37 to  $0.46 \mu\text{g vehicle}^{-1} \text{ km}^{-1}$ . The emission factors for other compounds ranged from 0.006 (acenaphthene) to 0.89 (pyrene)  $\mu\text{g vehicle}^{-1} \text{ km}^{-1}$  (Table S4). Pyrene (PYR) was the most abundant compound, followed by chrysene (CHR), benzo[ghi]perylene (BghiP) and benz[a]anthracene (BaA), which is different from biomass burning and coal combustion (Huang et al., 2014; Shen et al., 2012). PAHs diagnostic ratios have been used as a tool for identifying pollution emission sources including ANT / (ANT + PHE), FLA / (FLA + PYR), BaA / (BaA + CHR), BbF / (BbF + BkF), IcdP / (IcdP + BghiP) and BaP / (BaP + BghiP) (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002; Zhang et al., 2005). We summarized PAH ratios mentioned above in Fig. 2 for three combustion sources including vehicle emissions, biomass burning and coal combustion. On the whole, the six ratios in this study are similar to the other tunnel experiments, though environmental conditions of tunnels are different to some extent. It is also suggested that the ratio of FLA / (FLA + PYR) and IcdP / (IcdP + BghiP) might be more suitable to distinguish vehicle emissions from biomass burning and coal combustion.

Hopanes and steranes are known molecular markers of aerosol emissions from fossil fuel utilization (Simoneit, 1985). Rogge et al. (1993a) and Schauer et al. (1996) showed that these petroleum biomarkers can be used to trace motor vehicle exhaust contributions to airborne PM in the southern Californian atmosphere. Fourteen major hopanes homologues with emission factors in the range



**Figure 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. ANT: anthracene, PHE: phenanthrene, FLA: fluoranthene, PYR: pyrene, BaA: benz[a]anthracene, CHR: chrysene, BbF: benzo[b]fluoranthene, BkF: benzo[k]fluoranthene, BaP: benzo[a]pyrene, BghiP: benzo[ghi]perylene, IcdP: indeno[1,2,3-cd]pyrene. The vehicle emission composition is from data collected in roadway tunnels (this study; He et al., 2006, 2008; Ancelet et al., 2011; Ho et al., 2009; Oda et al., 2001). The biomass burning profiles are obtained from nine straws (Shen et al., 2011), 26 firewood (Shen et al., 2012), three plant leaves and branches (Sheesley et al., 2003) and two biomass burning briquettes (Sheesley et al., 2003). The coal combustion profiles are obtained from the average value of PAH ratios from the combustion of five coals (Shen et al., 2011) and main coal-mining regions in China (Zhang et al., 2008).

of  $0.46 \sim 9.14 \mu\text{g vehicle}^{-1} \text{km}^{-1}$  and 12 steranes homologues in the range of  $0.31 \sim 0.97 \mu\text{g vehicle}^{-1} \text{km}^{-1}$  were identified in this study.  $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane (HP30) was the most abundant component with the emission factor of  $9.14 \mu\text{g vehicle}^{-1} \text{km}^{-1}$ . The emission factor of total hopanes was  $32.0 \mu\text{g vehicle}^{-1} \text{km}^{-1}$ . Emissions of the S hopanes for the extended  $17\alpha(\text{H}), 21\beta(\text{H})$ -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 in the Supplement). Emission factors of individual sterane ranged from 0.31 to  $0.97 \text{ ng vehicle}^{-1} \text{km}^{-1}$ , and the sum of their emission factors was  $7.58 \mu\text{g vehicle}^{-1} \text{km}^{-1}$ . The most abundant homologue 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.

### 3.1.3 Stable carbon isotope

Stable carbon isotope analysis of vehicle emissions in Zhujiang tunnel yielded  $\delta^{13}\text{C}$  values ranging from  $-25.5$  to  $-24.7$ ‰ with an average value of  $-25.0 \pm 0.2$ ‰ and is comparable to previously reported ranges of  $-29$  to

$-24.6$ ‰ (Table 1) for vehicular fuel emissions. Generally, the variation in  $\delta^{13}\text{C}_{\text{Fuel}}$  could affect the  $\delta^{13}\text{C}$  of hydrocarbons (Keppler et al., 2004; Yamada et al., 2009). In the PRD region, the  $\delta^{13}\text{C}$  values of gasoline and diesel were on average  $-28.6 \pm 0.6$ ‰ and  $-27.8 \pm 0.2$ ‰; small variations of fuel  $\delta^{13}\text{C}$  were observed (Hu et al., 2014). We calculated the isotopic differences between  $\delta^{13}\text{C}_{\text{PM}_{2.5}}$  and  $\delta^{13}\text{C}_{\text{Fuel}}$ , which represent the apparent isotopic fractionation occurring during fuel burning. It expressed as  $\Delta^{13}\text{C}$  (‰) and is defined by the following equation (Yamada et al., 2009).

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

In this study, the value of  $\Delta^{13}\text{C}_{\text{PM}_{2.5}-\text{Fuel}}$  ranged from 2.7 to 3.5‰ with an average of 3.2‰, indicating that an isotopic fractionation occurred during fuel combustion. Comparing the stable isotopic carbon value of vehicular fuel emissions with other particulate emission sources (see Table 1), different emission sources showed different stable carbon isotopic composition. For total carbon in PM<sub>2.5</sub> samples,  $\delta^{13}\text{C}$  (‰) of coal and fuel oil combustion are  $-23.9$ ‰ and  $-26.0$ ‰, respectively, while that of vehicle emissions is  $-25.9 \sim -25.0$ ‰. Obviously, the  $\delta^{13}\text{C}$  (‰) of vehicle

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

Emission sources and sampling site	Particle types	$\delta^{13}\text{C}$ values	Sampling time	Reference
<b>Vehicle fuel emissions</b>				
Vehicle emissions (Zhujiang tunnel, China)	PM <sub>2.5</sub> / TC	$-25.0 \pm 0.3$	Aug 2013	This study
Vehicle emissions (tunnel of Rio de Janeiro, Brazil)	PM / OC	$-25.4$	Apr 1985	Tanner and Miguel (1989)
Vehicle emissions (tunnel of Rio de Janeiro, Brazil)	PM / EC	$-24.8$	Apr 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 <sub>2.5</sub> / OC	$-27.1$	N/A	L. Huang et al. (2006)
Vehicle emissions (Cassier tunnel, Canada)	PM <sub>2.5</sub> / EC	$-26.9$	N/A	L. Huang et al. (2006)
Diesel vehicle emissions (central Camionera del Norte, Mexico)	PM <sub>2.5</sub> / TC	$-24.6 \pm 0.3$	Mar 2002	Lopez-Veneroni (2009)
Gasoline vehicle emissions (tunnel of Avenida Chapultepec, Mexico)	PM <sub>2.5</sub> / TC	$-25.5 \pm 0.1$	Mar 2002	Lopez-Veneroni (2009)
Vehicle emissions (Mount Victoria tunnel, New Zealand)	PM <sub>2.5</sub> / TC	$-25.9 \pm 0.8$	Dec 2008 to Mar 2009	Ancelet et al. (2011)
<b>Non-vehicular fuel sources</b>				
Coal combustion (Paris, France)	PM <sub>2.5</sub> / TC	$-23.9 \pm 0.5$	May to Sep 2002	Widory et al. (2004)
Coal combustion (Yurihonjo, Japan)	PM <sub>2.5</sub> / EC	$-23.3$	N/A	Kawashima and Haneishi (2012)
Charcoal combustion (Yurihonjo, Japan)	PM <sub>2.5</sub> / EC	$-27.4 \pm 1.7$	N/A	Kawashima and Haneishi (2012)
Fireplace soot (Yurihonjo, Japan)	PM / EC	$-26.5 \pm 0.1$	N/A	Kawashima and Haneishi (2012)
Fuel oil combustion (Paris, France)	PM <sub>2.5</sub> / TC	$-26.0 \pm 0.5$	May to Sep 2002	Widory et al. (2004)
<b>Dust particles</b>				
Street dust (Mexico City, Mexico)	PM <sub>2.5</sub> / TC	$-21 \pm 0.2$	Mar 2002	Lopez-Veneroni (2009)
Street dust (Yurihonjo, Japan)	PM <sub>2.5</sub> / EC	$-18.4 \sim -16.4$	Nov 2009	Kawashima and Haneishi (2012)
<b>Biomass burning</b>				
C4 plant	PM / TC	$-13 \pm 4$	N/A	Boutton (1991)
C4 plant (Yurihonjo, Japan)	PM <sub>2.5</sub> / EC	$-19.3 \sim -16.1$	Apr to Nov 2009	Kawashima and Haneishi (2012)
C3 plant	PM / TC	$-27 \pm 6$	N/A	Boutton (1991)
C3 plant (Yurihonjo, Japan)	PM <sub>2.5</sub> / EC	$-34.7 \sim -28.0$	Apr to Nov 2009	Kawashima and Haneishi (2012)

**Table 2.** Vehicle emission standards and limits for PM and NO<sub>x</sub> implemented in Guangzhou after 2000.

Emission standard	Year <sup>a</sup>	Limit for PM		Limit for NO <sub>x</sub>	
		g km <sup>-1</sup> <sup>b</sup>	g kWh <sup>-1</sup> <sup>c</sup>	g km <sup>-1</sup> <sup>b</sup>	g kWh <sup>-1</sup> <sup>c</sup>
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

<sup>a</sup> Year of implementation; <sup>b</sup> for light-duty vehicles; <sup>c</sup> for compression ignition and gas-fueled positive ignition engines of vehicles.

emissions is not significantly different from that of coal and fuel oil combustion. However, they are obviously different from other sources, like dust particles ( $-21 \sim -18.4\%$ ), C3 plants ( $-19.3 \sim -13\%$ ) and C4 plants ( $-34.7 \sim -27\%$ ). Therefore,  $\delta^{13}\text{C}$  might be used to distinguish the fossil fuel combustion from other sources.

### 3.2 Comparison to previous studies conducted in the same tunnel

To investigate the variation of chemical emission characteristics from vehicles in the PRD region over the past decade, we compared the chemical emission characteristics of this study to that of previous study (He et al., 2008) for the same tunnel in 2004 (see Figs. 3 and 4). Figure 3 shows that PM<sub>2.5</sub> mass, OC and EC decreased significantly from 2004 to 2013. The

reason can be partly attributed to the implementation of pollution control measures for Chinese vehicle emissions. During this 9-year period, vehicle emission standards have raised two levels (from China II in 2004 to China IV in 2013) (Table 2). Additionally, comparing the fleet composition of 2013 to 2004 in Zhujiang tunnel, we found that the proportion of DV and GV decreased while LPGV increased. LPG is a type of clean energy, and LPGV is known to emit much less PM mass than GV and DV (Allen et al., 2001; Myung et al., 2014; Yang et al., 2007). LPG could be combusted more completely than gasoline and diesel. Changes mentioned above contributed greatly to the decrease of emission factors of OC and EC (31.3 and 66.9 %) and PM<sub>2.5</sub> mass (16.0 %) from 2004 to 2013. However, the emissions of PM<sub>2.5</sub> mass, OC and EC are still significantly higher than those measured in

**Table 3.** Vehicle fuel standards and limits for sulfur content (mg kg<sup>-1</sup>) implemented in Guangzhou after 2000.

Standard	China I		China II		China III		China IV	
	limit	year <sup>a</sup>	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 <sup>b</sup>	2003	–	–	50	2013

<sup>a</sup> Year of implementation; <sup>b</sup> unit: mg m<sup>-3</sup>.

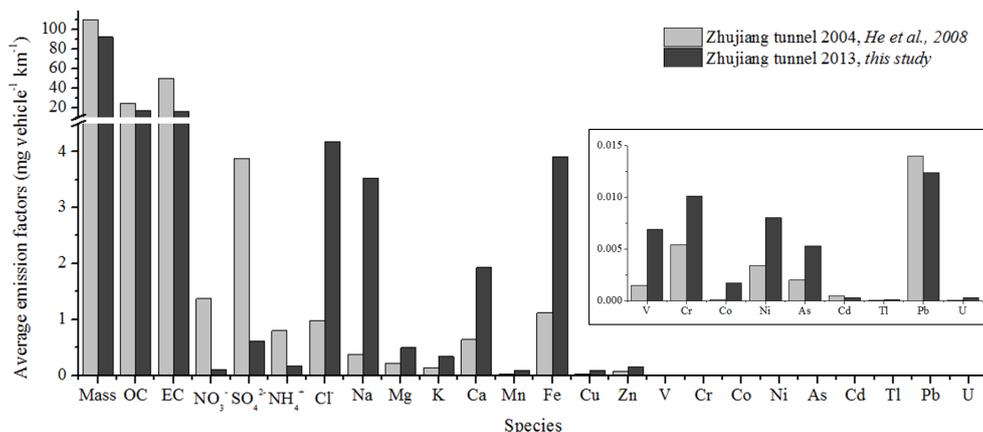
other countries (see Table S5). The implication of these high emission levels is that both the fuel quality and engine technologies in the PRD region need to be further improved.

It is also found from Fig. 3 that emission factors of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> decreased from 2004 to 2013. Improvement of fuel quality resulted in decreasing of sulfate emission factor from 3.87 to 0.61 mg vehicle<sup>-1</sup> km<sup>-1</sup>, since the amount of sulfur in fuel is slashed by 81.5 ~ 95 % in China IV (2013) compared to that in China II (2004) (Table 3). The emission levels of nitrate and ammonium were about one-tenth of those observed in 2004, possibly because NO<sub>x</sub> emission standards tightened from 2004 to 2013 (Table 2), leading to lower production of ammonium nitrate. The emission factor of chloride is significantly higher than that obtained from Zhujiang tunnel in 2004 and other tunnels. Chloride was found up to 74 mg vehicle<sup>-1</sup> km<sup>-1</sup> in PM<sub>10</sub> 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. The good correlation between Cl<sup>-</sup> and Na<sup>+</sup> ( $r^2 = 0.992$ ) indicates that resuspension of sea salt particles combined with vehicle emission PM might be a major source (He et al., 2008).

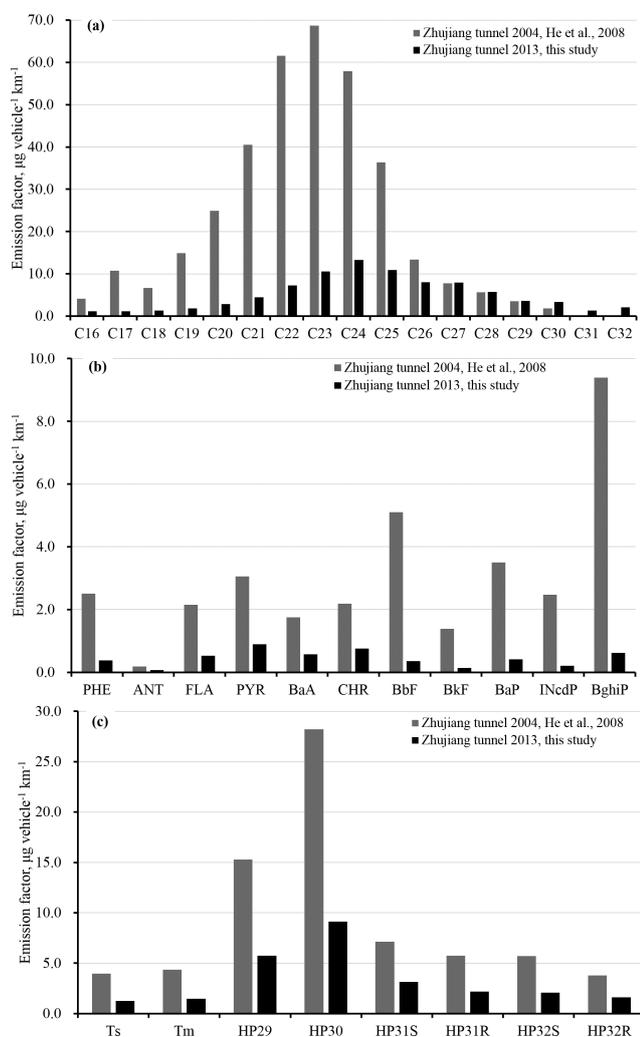
Emission factors of most of the metal elements increased in Zhujiang tunnel from 2004 to 2013 with the exception of Cd and Pb. Na emissions increased 3.16 mg vehicle<sup>-1</sup> km<sup>-1</sup> in 2013 from 2004. Na correlated weakly with Cl<sup>-</sup> ( $r^2 = 0.374$ ) and Na<sup>+</sup> ( $r^2 = 0.429$ ). This indicates that Na emissions had other sources and was not only from the resuspension of sea salt particles. The other four most abundant elements including Fe, Ca, Mg and K increased 1 to 3 times, probably because of resuspended road dust. However, the wind speed in 2013 was not found to be significantly higher than that in 2004 (3.8 m s<sup>-1</sup> in 2013 vs. 3.0 m s<sup>-1</sup> 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 also cause the increased emissions of these elements, such as oil additives (Mg, Ca, Cu, Zn) (Cadle et al., 1997), the wear of engines (Fe) (Cadle et al., 1997; Garg et al., 2000) and 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 0.5 to 4.5 times. Although the sum of these elements did not exceed 0.5 % of PM<sub>2.5</sub> mass, they are important for health effects. Lower emission factors of Pb (0.01 ± 0.0007 mg vehicle<sup>-1</sup> km<sup>-1</sup>) in 2013 than in 2004 could be a result of the phasing out of leaded gasoline across China in the late 1990s.

Figure 4 shows a comparison of organic compound emissions in Zhujiang tunnel between 2004 and 2013. The *n*-alkane homologues exhibited a smooth hump-like distribution with the most abundance at C24, as shown in Fig. 4a. Such a distribution pattern was similar to patterns observed in Zhujiang tunnel in 2004. However, there are some differences. Firstly, the highest abundant *n*-alkane shifted from C23 in 2004 to C24 in 2013. This difference might be explained by the shift of gas–particle partitioning as alkanes of <C26 are semi-volatile. However, the *t* test showed that the temperatures were not significantly different ( $p = 0.14$ ) between this study (33.0 ± 2.3 °C) and that in 2004 (31.8 ± 1.0 °C). Thus, the differences of C<sub>max</sub> cannot be regarded as a result of temperature differences. Furthermore, C<sub>max</sub> was found to be C24 in every test of this study although the temperature ranged from 28.6 to 36.1 °C. It was reported that the *n*-alkane in the highest abundance was C20 for DV and C25 or C26 for GV in dynamometer tests (Rogge et al., 1993a; Schauer et al., 1999, 2002). As the emissions collected in tunnel studies present a composite result of emissions from a mixed vehicle fleet, the lower fraction of DV in 2013 was more likely the cause of the shift of C<sub>max</sub>. Secondly, emission factors of C16–C26 in 2013 were significantly lower than those in 2004, while this trend reversed gradually after C27. Emission factors of the PAHs decreased by 67.6 ~ 93.4 %. BaP equivalent emission factors decreased by 88.1 % from 2004 to 2013 (Table S6). This could be attributed to the variation of fleet composition between 2004 and 2013. PAHs emitted from LPGV are about one-third of that from GV (Yang et al., 2007), while DV emit more PAHs than GV (Phuleria et al., 2006). Therefore, the higher proportion of LPGV and lower proportion of DV resulted in the lower emission factor of PAHs in 2013 than that in 2004. Emission factors of hopanes also decreased from 2004 to 2013; the percentage of decrease ranged from 56.2 to 68.7 %. However, the distributions of hopane series derived from dif-



**Figure 3.** Comparison of PM<sub>2.5</sub>, OC, EC, WSII and metal emissions in Zhujiang tunnel sampling in 2004 and 2013.

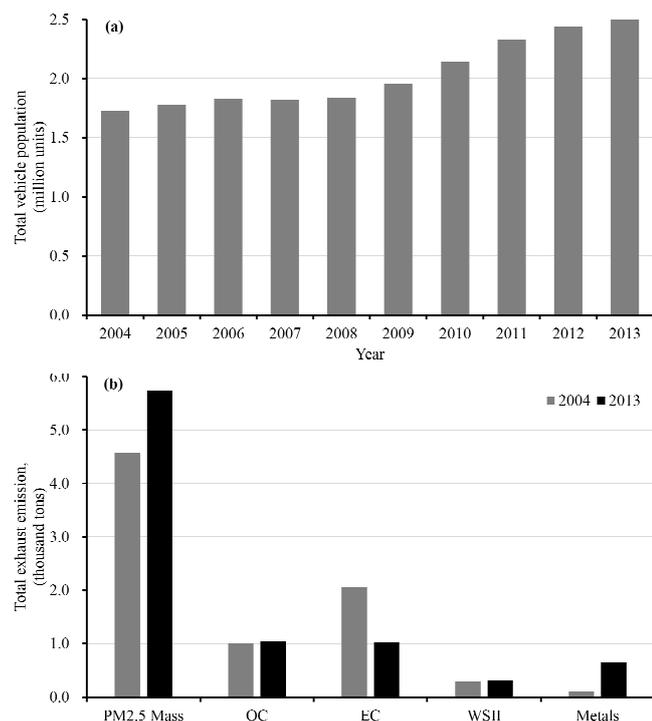


**Figure 4.** Comparison of organic compounds emissions in Zhujiang tunnel sampling in 2004 and 2013.

ferent tunnel studies were very similar (see Fig. S1). This suggests that the hopane emission characteristics might be independent of the fleet composition. This is a reasonable result given that hopanes originate from the lubricating oil used in DV, GV and LPGV rather than from the fuel (He et al., 2008; Phuleria et al., 2006). Owing to the fact that more units in heavy-duty vehicles need lubrication, emission factors of hopanes attributable to heavy-duty vehicles were higher than those attributable to light-duty vehicles (Phuleria et al., 2006). Reduction of the proportion of heavy-duty vehicles (buses, heavy-duty trucks, large passenger cars) in fleet composition in 2013 (11.3 %) compared to that in 2004 (20 %) might be the reason that emission factors of hopanes decreased.

### 3.3 Implications for vehicle emission control policy

Vehicle emission control strategies and policies adopted by Guangdong province can be classified as emission control on vehicles, fuel-quality improvements and alternative fuel utilization. PM emission standards for newly registered vehicles were tightened from China II in 2004 to China IV in 2013 (Table 2). The reduction of on-road high-PM-emitting vehicles, the phasing in of lower-PM-emitting vehicles and more environmentally friendly on-road vehicles with more advanced engines following the implementation of these emission standards were effective for decreasing PM emissions. Emission factors of PM decreased by 16 % from 2004 to 2013. Also for NO<sub>x</sub>, the emission limit was reduced to about half from 2004 to 2013. This change in emission standards that limit NO<sub>x</sub> emissions is a major factor in the decrease of emission factors of nitrate and ammonium by about 90 %. Additionally, the national standards have been revised several times to improve fuel quality to adapt to stringent vehicle emission standards (Table 3). Sulfur content, for example, showed a sharp decrease by over 90 % from 2004 to 2013, resulting in the decrease of the emission factor of sulfate by 70 %. LPG and liquefied natural gas have grad-



**Figure 5.** (a) Growth in total vehicle population in Guangzhou during 2004–2013. (b) Total exhaust emissions of PM<sub>2.5</sub> mass, OC, EC, WSII and metal in 2004 and 2013.

ually taken the place of diesel and gasoline as the fuel of taxis and buses after 2004; these vehicles now seldom use diesel and gasoline as fuel (<http://www.southcn.com/news/gdnews/nanyuedadi/200707040173.htm>). The application of clean fuel led to nearly complete combustion and resulted in much lower emissions from taxis and buses. In general, our results suggest that these strategies are effective to reduce emission factors of PM<sub>2.5</sub> mass, as well as OC, EC, WSII and organic compounds in PM<sub>2.5</sub>. However, the total vehicle population increased year by year. As shown in Fig. 5a, the total vehicle population increased by 49.1 % from 2004 to 2013. Total emissions of vehicle exhaust of PM<sub>2.5</sub> mass (calculated as emission factors multiply by annual average driving distance per car and vehicle population; Wu et al., 2012) increased by 25.2 % from 2004 to 2013 (Fig. 5b). Consequently, it is demonstrated that more stringent emission standards are higher quality of fuel and more utilization of clean fuels are necessary to offset the impacts induced by the growth in vehicle population and to improve air quality in the PRD region. Additionally, owing to a lack of mandatory national standards limiting metal content in vehicle emissions, the emissions of the majority of metals increased from 2004 to 2013 (Figs. 3 and 5b). In China, heavy metals, including As, Cr, Cu, Ni and Tl, are listed as key substances to be preferentially monitored in the atmospheric environment (SEPA, 2003); thus, the increase of metal elements should raise the awareness of the government due to their health concern.

## 4 Conclusions

PM<sub>2.5</sub> samples were collected between 10 and 14 August 2013 in Zhujiang tunnel, Guangzhou, to acquire a comprehensive snapshot of the chemical characteristics of vehicle emissions. The average emission factors of PM<sub>2.5</sub> mass, EC, OC, WSOC, WSII, metal elements, organic compounds and stable carbon isotope were measured. Stable carbon isotope  $\delta^{13}\text{C}$  values indicate that an isotopic fractionation of 3.2 ‰ occurred during fuel combustion. Compared to a previous study in Zhujiang tunnel in 2004, emission factors of PM<sub>2.5</sub> mass, EC, OC and major WSII decreased due to control-policy-induced changes from 2004 to 2013: change of fleet composition, implementation of more stringent gasoline and diesel emission standards, improvement in fuel quality and clean fuel used for taxis and buses. The shift in *n*-alkanes distribution and decreased PAHs emissions were due to the lower proportion of DV in 2013 than in 2004, and the decrease in emission factors of hopanes was due to the reduction of the proportion of heavy-duty vehicles. Our study shows that control policies for vehicles emissions by the government were effective to decrease the emission factors of PM<sub>2.5</sub>, EC, OC and WSII from on-road vehicular fleets. However, the increase in emissions 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 of the growth of the vehicle population and to improve air quality in the PRD region, more stringent and aggressive emission control policies are necessary.

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