

# Emission factors of PM species based on freeway measurements and comparison with tunnel and dynamometer studies

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## Abstract

Emission factors of various particle species from light- and heavy-duty vehicles (LDVs and HDVs, respectively), including organic and elemental carbon (OC and EC), sulfate, polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, trace metals, elements, and particle number (PN), were estimated based on roadway measurements. Sampling campaigns were conducted at two different roadways: the CA-110 highway (where only gasoline-powered vehicles are allowed), and the I-710 freeway (where about 20% of the total number of vehicles are diesel-powered trucks). The particulate matter (PM) emission factors determined in these roadways were compared to those reconstructed from recent source emission data from the Caldecott tunnel [Phuleria, H.C., Geller, M.D., Fine, P.M., Sioutas, C., 2006. Size-resolved emissions of organic tracers from light- and heavy-duty vehicles measured in a California roadway tunnel. *Environmental Science and Technology* 40 (13), 4109–4118], and those from previous tunnel and chassis dynamometer studies. Very good agreement between estimated and reconstructed emission factors was found for PN, EC, sulfate, high-molecular-weight (MW) PAHs, hopanes and steranes. This suggests that PM-speciated chemical data collected at roadsides can be used to calculate reliable emission factors for several important particle species at other locations characterized by a similar mix of on-road motor vehicles. The agreement between our results and other studies in the emission factors of trace elements and metals varied from very good (for species such as Cu, Mo, Ba, Pb) to poor (for species such as Mg, Fe, Ca), probably because the atmospheric concentrations of the latter elements are associated with both traffic and non-traffic sources, and the relative abundances of Mg, Ca, and Fe in road dust varies considerably across locations. The emission factors of OC and EC were clearly the highest for HDVs, and those of PAHs, hopanes, and steranes from our roadway measurements were well within the range of values reported in the literature from tunnel and dynamometer studies. The approach presented in this paper allows for a straight-forward estimation of PM emission factors from ambient, near-freeway measurements. Although the uncertainties inherent in the method proposed here must be acknowledged (e.g. assumptions were made to estimate the average fleet composition and the total carbon content in the vehicles' exhaust), our results are generally in very good agreement with those in the available literature for most non-labile PM species.

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## 1. Introduction

Numerous epidemiological studies have found positive associations between adverse respiratory and cardiovascular effects and exposure to atmospheric particulate matter (PM) (Samet et al., 2000; Pope et al., 2002; USEPA, 2004). In addition, toxicological experiments on human volunteers, laboratory animals, and tissues have provided some evidence of adverse effects for ultrafine particles (aerodynamic diameter  $<0.1\text{--}0.2\text{ }\mu\text{m}$ ) and outdoor fine PM ( $\text{PM}_{2.5}$ ; aerodynamic diameter  $<2.5\text{ }\mu\text{m}$ ) (Oberdorster et al., 2004; Nel, 2005). Although the biological mechanisms responsible for the toxicity of PM are still uncertain, researchers have recently attempted to link the toxicity of PM with several of its chemical components, including organic and elemental carbon (OC and EC, respectively) (Mar et al., 2000; Metzger et al., 2004), trace metals (Saldiva et al., 2002; Wellenius et al., 2003) and polycyclic aromatic hydrocarbons (PAHs) (Dejmek et al., 2000).

In urban environments, light- and heavy-duty vehicles (LDVs and HDVs) have become the major source of ultrafine, fine and in some cases coarse PM (Gertler et al., 2000) via fuel combustion, mechanical and tire wear, and secondary aerosol formation from chemical reactions involving both organic and inorganic gaseous precursors (Schauer et al., 1996; Mysliwiec and Kleeman, 2002). It is therefore essential to characterize and quantify vehicle emissions in order to evaluate the impact on human health and the environment, and also to assess the overall effectiveness of exhaust control technologies.

Different approaches have been used to characterize vehicular emissions, including chassis dynamometer tests (Schauer et al., 1999, 2002; Zielinska et al., 2004; Riddle et al., 2007a,b; Fujita et al., 2007), roadway tunnel studies (Geller et al., 2005; Phuleria et al., 2006; Lough et al., 2005) and roadside pollutants concentration measurements (Kuhn et al., 2005a; Ntziachristos et al., 2007a). Chassis dynamometer experiments have the ability to examine vehicle emissions under different driving/loading settings and to effectively evaluate exhaust control technologies. However, a controlled laboratory environment may not necessarily be representative of real-world driving conditions (Zhang and Morawska, 2002), and non-tailpipe emissions such as those from tire wear, the wear of brake linings and re-suspended road dust (Allen

et al., 2001) are not accounted for by these types of studies. Roadway tunnel experiments characterize a large portion of all on-road vehicles, providing a detailed analysis of the overall vehicle fleet emissions (Phuleria et al., 2006). However, a limitation of these studies is that they provide information that is specific to a particular tunnel under restricted driving conditions. Thus, these results may not be broadly applicable to open roadways. Finally, although roadside pollutant concentration measurements characterize freeways emissions under actual ambient and driving conditions well, they may be influenced by changes in the local meteorological and environmental conditions (Ntziachristos et al., 2007b). This could complicate a direct comparison of the pollutant levels at different locations.

In the present study, the concentrations of several gas- and particle-phase species were measured near two major roadways in the Los Angeles Basin and at selected background sites to determine fuel-based roadway emission factors for specific PM components (i.e. OC, EC and sulfur), organic constituents (PAHs, hopanes and steranes), trace metals and elements, and particle number (PN). The calculated factors were compared to those reported in previous works, as well as those reconstructed from size-segregated emission profiles obtained at the Caldecott tunnel, California, by Geller et al. (2005) and Phuleria et al. (2006). Our study thus provides a convenient methodology to derive emission factors for PM species that can be used to characterize on-road motor vehicle emissions under real-world driving conditions. This information is crucial in evaluating the effectiveness of emission control strategies and legislature, as well as in assessing PM exposure from roadway traffic emissions.

## 2. Experimental methods

### 2.1. Sampling locations

The present study was carried out near two major freeways in the Los Angeles Basin, the California State Highway (CA-110) and the Long Beach Freeway (I-710). The former connects Pasadena to downtown Los Angeles, where it merges into the I-110, which runs southbound towards San Pedro and represents one of the main freeways in the Los Angeles County. Only light-duty gasoline-powered vehicles are allowed on the CA-110. The sampling site was located downwind of the highway at 3 m from the edge of the northbound lanes on the east

(downwind) side. A background site was also set up about 150 m downwind of the highway. Samples near the CA-110 were collected daily (from 12:00 pm to 07:00 pm and only on weekdays) during two different campaigns that took place in the summer of 2004 (May–June 2004) and in the winter (January) of 2005 (Kuhn et al., 2005a). During the sampling period, the average traffic density was estimated to be 5700 vehicles  $\text{h}^{-1}$  in the summer and 5100 vehicles  $\text{h}^{-1}$  in the winter; the average vehicle speed was about 112  $\text{km h}^{-1}$  in both seasons (Kuhn et al., 2005a, b).

The I-710 is a 26 m wide, eight-lane freeway connecting the ports complex of Long Beach and San Pedro to the shipping yards in East Los Angeles. The sampling site was located in a paved property, 3 m downwind of the edge of the freeway and away from the influence of any other immediate PM sources, while the background site was set up about 1.6 km downwind of the freeway. Samples were collected daily (from 10:00 am to 05:00 pm and only on weekdays) during 7 weeks between February and April, 2006 (Ntziachristos et al., 2007a). The average traffic volume and vehicle speed at the I-710 were about 5400 vehicles  $\text{h}^{-1}$  and 81  $\text{km h}^{-1}$ , respectively (Kuhn et al., 2005a, b). The majority of the freeway traffic is comprised of light-duty gasoline-powered cars and, typically, about 20% of the total number of vehicles is represented by heavy-duty-diesel-powered trucks (Ntziachristos et al., 2007a, b).

## 2.2. Sampling and analysis

Similar sampling sites were set up at both the CA-110 and the I-710, and at the corresponding background locations to monitor the same species concentrations and weather information concurrently. Ambient carbon dioxide ( $\text{CO}_2$ ) was measured continuously (1 min) using handheld air monitors (Q-Trak Plus Model 8554, TSI Inc., St. Paul, Minnesota). Continuous (1 min) ambient PN concentrations were measured using condensation particle counters (CPC, Model 3022A, TSI Inc., St. Paul, MN). Two micro-orifice uniform deposit impactors (MOUDI) (MSP, Inc., Minneapolis, MN) ( $301 \text{ min}^{-1}$ ) and two tri-mode high-volume impactor samplers ( $4501 \text{ min}^{-1}$ ) were also deployed to collect size-segregated ambient aerosol filter samples. For the MOUDI, 47 mm PTFE Teflon filters ( $2 \mu\text{m}$  pore, Gelman Science, Ann Arbor, MI), were used as impaction

substrates for coarse ( $\text{PM}_{10}$ – $\text{PM}_{2.5}$ ) and accumulation ( $\text{PM}_{2.5}$ – $\text{PM}_{0.18}$ ) mode PM, and a 37 mm PTFE Teflon filter ( $2 \mu\text{m}$  pore, Gelman Science, Ann Arbor, MI) was used to collect quasi-ultrafine PM ( $\text{PM}_{0.18}$ ). For the hi-volume samplers, coarse, accumulation and ultrafine PM were collected on a 47 mm quartz fiber impaction substrate (Whatman Grade QM-A 1851-047, Whatman Inc., Florham Park, NJ), quartz fiber impaction strips, and a 203 mm  $\times$  254 mm quartz fiber filter (Pallflex Tissu-quartz 2500QAT-UP-8\_10, Pall Corp, East Hills, NY), respectively. All quartz substrates and filters were pre-baked at 550  $^{\circ}\text{C}$  for 12 h and stored in baked aluminum foil prior to deployment.

Gravimetric concentrations were determined by weighing the Teflon filters from the MOUDI before and after sampling using a microbalance (Model MT-5, Mettler Toledo Inc., Highstown, NJ) after allowing 24 h for equilibration at a temperature of 22–24  $^{\circ}\text{C}$  and a relative humidity of 40–45%. The filter-samples collected at the CA-110 site were further analyzed by means of X-ray fluorescence analysis (XRF) for metals and other trace elements (Teflon filters), and by ion chromatography to determine the concentrations of sulfate and nitrate (quartz filters). Similarly, the MOUDI filter-samples collected at the I-710 site were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) (Lough et al., 2005; Sheesley et al., 2005) and ion chromatography to determine the element and trace metal content, and the inorganic sulfate and nitrate concentrations, respectively. Portions of all Hi-Volume quartz filters/substrates collected at both roadway-sites were analyzed for OC and EC by the thermal desorption/optical transmission analysis (Sunset Laboratory Inc., Tigard, OR) (Birch and Cary, 1996), and for individual organic compounds/tracers concentrations by following a well established solvent-extraction/molecular quantification analysis protocol (Phuleria et al., 2006). At all locations wind direction/speed, temperature and humidity were recorded with a weather station (Wizard III, Weather Systems Company, San Jose, CA, USA).

## 2.3. Emission factors from roadway measurements

A fuel-based emission factor for pollutants is defined as the mass or number of pollutant emitted per mass of fuel consumed (Miguel et al., 1998; Kirchstetter et al., 1999). Since gasoline engine combustion efficiencies in normal driving conditions

are higher than 90% (this value is even higher for diesel engines), it is reasonable to assume that the carbon mass in the vehicle's exhaust is mostly in the form of  $\text{CO}_2$  and that the contribution of CO and other carbon-containing compounds to the total emitted carbon mass is negligible (Yli-Tuomi et al., 2005). Thus, the emission factor of a generic pollutant can be written as

$$E_P = 10^3 \left( \frac{[P]_{\text{fw}} - [P]_{\text{bg}}}{[\text{CO}_2]_{\text{fw}} - [\text{CO}_2]_{\text{bg}}} \right) w_c, \quad (1)$$

where  $E_P$  is the emission factor for the pollutant  $P$  ( $\text{g kg}^{-1}$  of fuel burned, or number count  $\text{kg}^{-1}$  of fuel burned).  $[P]$  is the mass or number concentration of the pollutant of interest ( $\text{g m}^{-3}$ , or number count  $\text{m}^{-3}$ ).  $[\text{CO}_2]$  is the concentration of  $\text{CO}_2$  in  $\mu\text{g}$  of carbon  $\text{m}^{-3}$ . The subscripts fw and bg indicate freeway and background sites, respectively.  $w_c$  is the weight fraction of carbon in the considered fuel and it has been reported to be 0.87 for diesel and 0.85 for gasoline (Geller et al., 2005; Phuleria et al., 2006). Similar emission factor equations have also been used by Kirchstetter et al. (1999), Phuleria et al. (2006) and Yli-Tuomi et al. (2005) to estimate  $E_P$  in tunnel environments and freeways. In our study, emission factors were calculated directly from pollutant concentrations measured in the proximity of the roadways and at background locations. It should be noted that emission factors estimated using Eq. (1) are highly uncertain for species that are not characterized by substantial roadways emissions, when their concentrations are similar both at freeway and at background sites. These species are not an important part of the roadway emission profile, and their emission factors should be interpreted with caution. All roadway and background concentrations measured during this study are reported in the Supplemental Information document. For the CA-110 site, a value of 0.85 was used as the carbon weight fraction for gasoline since all vehicles on the highway are gasoline fuelled. For the I-710 site, the carbon weight fraction was adjusted for the fraction of operating diesel vehicles (around 20% of the total on-road fleet), yielding a value of 0.854 (Ntziachristos et al., 2007b).

#### 2.4. Reconstructed emission factors

Based on information about heavy-duty-diesel and light-duty-gasoline vehicles (HDV and LDV, respectively), reconstructed roadway emission fac-

tors for the pollutants of interest can be obtained according to the following equation:

$$E_{P,\text{rec}} = f_{\text{HDV}} E_{P,\text{HDV}} + f_{\text{LDV}} E_{P,\text{LDV}}, \quad (2)$$

where  $E_{P,\text{rec}}$  represents the expected mixed-fleet emission factor for the pollutant  $P$  ( $\text{g}$  of PM species  $\text{kg}^{-1}$  of fuel burned, or particle number  $\text{kg}^{-1}$  of fuel burned);  $f_{\text{HDV}}$  and  $f_{\text{LDV}}$  are the on-road fractions of HDV and LDV, respectively. For the I-710 freeway,  $f_{\text{HDV}} = 20\%$  and  $f_{\text{LDV}} = 80\%$ . For the CA-110 highway, we assumed that 100% of the on-road fleet was represented by LDV ( $f_{\text{LDV}} = 100\%$ ).  $E_{P,\text{HDV}}$  and  $E_{P,\text{LDV}}$  are the emission factors of pollutant  $P$  for HDV and LDV, respectively, and were obtained from data collected during a study conducted at the Caldecott tunnel in 2004 (Geller et al., 2005; Phuleria et al., 2006). The large population of mixed vehicles under real-world driving conditions in the tunnel has provided the most representative and up to date source emission profiles data available in California.

In addition, the emission factors from roadway measurements were used to reconstruct the HDV fleet emission factors ( $E_{\text{HDV},\text{rec}}$ ) using the following equation:

$$E_{\text{HDV},\text{rec}} = \frac{E_{710} - f_{\text{LDV}} E_{\text{LDV}}}{f_{\text{HDV}}}, \quad (3)$$

where  $E_{710}$  is the emission factor at the I-710 freeway,  $E_{\text{LDV}}$  is the LDV fleet emission factor and was assumed to be equal to that obtained at the CA-110 highway, because the fraction of LDVs there is virtually 100%.  $f_{\text{LDV}}$  and  $f_{\text{HDV}}$  are the fractions of LDVs and HDVs at the I-710 freeway (0.8 and 0.2, respectively).

### 3. Results and discussion

#### 3.1. Comparison of roadway and reconstructed tunnel emission factors for particle number, $\text{PM}_{2.5}$ mass, and particle species

Table 1 presents average emission factors ( $E_P$ ) for PN,  $\text{PM}_{2.5}$  mass, OC, EC and sulfate estimated at CA-110 and I-710 sites (only  $E_P$  values in the fine,  $d_p < 2.5 \mu\text{m}$ , range are shown). Although the traffic volumes at both roadways were similar during the study period, the  $E_{\text{PN}}$  at the I-710 freeway was about 1.8 times higher than that at the CA-110 highway. Similarly, fine and ultrafine  $E_{\text{EC}}$  estimates were about 5.5 times higher at the I-710 site than at the CA-110 site. These results highlight

Table 1

Emission factors (expressed in  $\text{mg kg}^{-1}$  of fuel burned, or particle  $\# \text{kg}^{-1}$  of fuel burned) of particle number (PN),  $\text{PM}_{2.5}$  mass, organic and elemental carbon (OC and EC, respectively), sulfate and metals at the CA-110 and the I-710 sites

	CA-110		I-710	
	Average	SD	Average	SD
Particle number ( $\# \text{kg}^{-1}$ )	$1.8 \times 10^{15}$	$2.5 \times 10^{14}$	$3.3 \times 10^{15}$	$1.1 \times 10^{15}$
$\text{PM}_{2.5}$ mass ( $\text{mg kg}^{-1}$ )	113.6	25.9	219.0	39.1
$\text{PM}_{2.5}$ species ( $\text{mg kg}^{-1}$ )				
OC	105.5	22.1	205.9	48.8
EC	20.5	4.9	110.1	13.7
Sulfate	5.4	1.8	8.3	4.9
$\text{PM}_{2.5}$ metals ( $\text{mg kg}^{-1}$ )				
Mg	0.08	0.04	0.23	0.09
P	—	—	0.13	0.04
S	—	—	2.83	0.99
K	0.09	0.07	0.19	0.05
Ca	0.17	0.09	0.56	0.24
V	—	—	0.02	0.01
Mn	0.03	0.01	0.01	0.01
Fe	2.41	0.17	1.68	0.61
Ni	—	—	0.01	0.01
Cu	0.18	0.01	0.08	0.03
Zn	—	—	0.07	0.03
Mo	0.01	0.01	0.01	0.01
Ba	0.4	0.06	0.28	0.1
Pb	—	—	0.02	0.01

the dominant contribution of diesel vehicles to ambient PN and EC concentrations and are supported by emission factors data for HDV and LDV from previous studies referenced earlier. Furthermore, the  $E_{\text{OC}}/E_{\text{EC}}$  ratio for the fine fraction of PM was 5.2 and 1.9 at the CA-110 and I-710 sites, respectively, which confirms the important contribution of diesel vehicles emissions to ambient EC. The relatively high emission factors for OC may be due, at least in part, to the effect of positive artifacts caused by adsorption of organic vapors in the sampling quartz fiber filter (Mader and Pankow, 2002).  $E_{\text{sulfate}}$  was higher at the I-710 site than at the CA-110 site, probably because of the greater fraction of HDVs, which are known to emit higher amounts of sulfate due to the elevated sulfur content of their fuels (Phuleria et al., 2006).

Fig. 1 shows a comparison between the average emission factors of  $\text{PM}_{2.5}$  mass, EC, sulfate and PN, estimated ( $E_{\text{p}}$ ) and reconstructed ( $E_{\text{p,rec}}$ ) from data collected at the I-710 site (Fig. 1a), and at the CA-110 site (Fig. 1b). Error bars represent the standard deviation of the emission factors based on individual samples collected during this study. Although roadway environments tend to be sub-

stantially more affected by ambient conditions such as rapid air dilution and atmospheric dispersion than tunnels, the emission factors obtained at both the CA-110 and the I-710 sites show reasonable agreement with those reconstructed from tunnel measurements. The  $E_{\text{PN}}/E_{\text{PN,rec}}$  ratios were 0.91 and 0.72 for the I-710 site and the CA-110 site, respectively. The somewhat higher  $E_{\text{PN,rec}}$  estimates may be the result of coagulation of ultrafine particles emitted by vehicles inside the more confined tunnel environment (Zhu et al., 2002). This is less likely to occur at ambient conditions, when particle dispersion is maximized. Similar results were also found for fine EC, which  $E_{\text{EC}}/E_{\text{EC,rec}}$  ratios were 0.70 and 0.67 at the CA-110 and the I-710 sites, respectively. It is important to note that the higher levels at the latter location may also be due to the uphill driving, which has a substantial effect on the engine load (Maricq et al., 1999; Kittelson et al., 2004). Using typical values for road resistance and solving the equation of motion for LDVs and HDVs Ntziachristos et al. (2007a) calculated that a positive road gradient of 4.2% in the Caldecott tunnel corresponds to 1.6 and 2.9 times increase in engine load for LDVs and HDVs, respectively. The same study showed that PN and



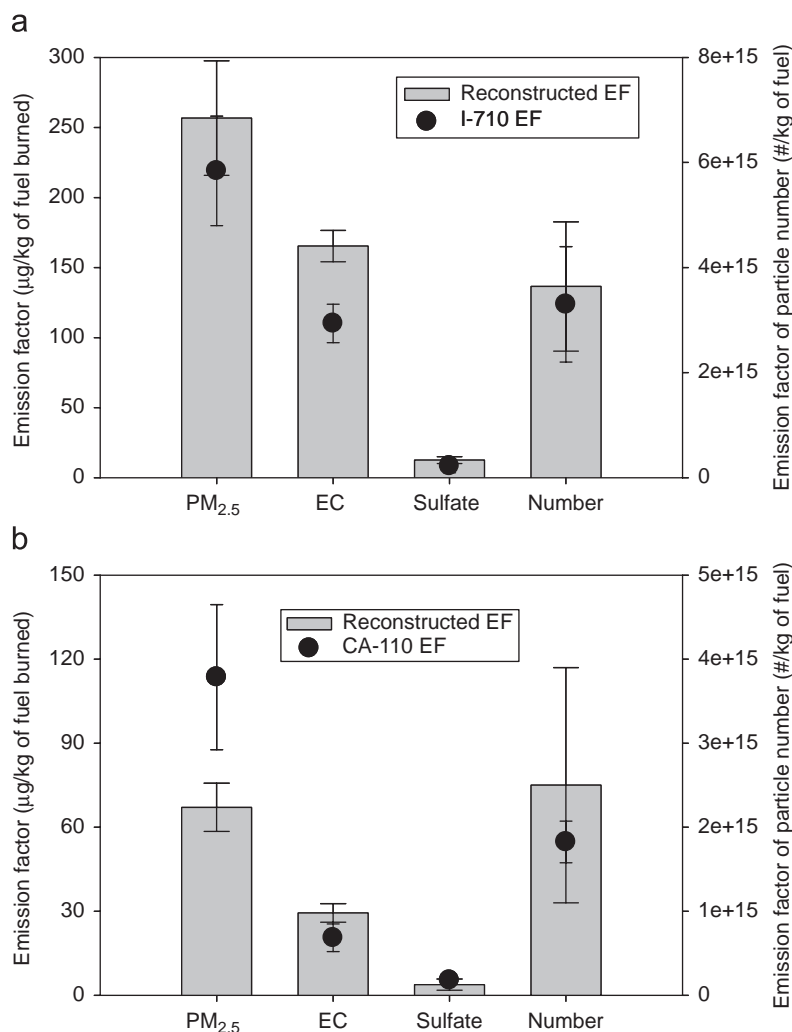


Fig. 1. Comparison among measured and reconstructed emission factors (in  $\mu\text{g kg}^{-1}$  of fuel burned, or particle #/kg of fuel burned) of PM<sub>2.5</sub> mass, elemental carbon (EC), sulfate and particle number (PN) from the I-710 freeway (a) and the CA-110 highway (b).

black carbon (BC) concentrations in the tunnel were at the same, or slightly higher levels than next to the I-710 freeway, despite the much lower fraction of diesel vehicles in the former environment. The effect of engine load on PN emissions is more substantial in gasoline engines, but does increase BC emissions in both LDVs and HDVs (Zielinska et al., 2004). The  $E_{\text{sulfate}}/E_{\text{sulfate,rec}}$  and  $E_{\text{PM}_{2.5}}/E_{\text{PM}_{2.5,rec}}$  ratios were higher at the CA-110 site (1.41 and 1.67 for sulfate and PM<sub>2.5</sub>, respectively) than at the I-710 site (0.66 and 0.85 for sulfate and PM<sub>2.5</sub>, respectively). The reasons for this discrepancy remain unclear, but estimated and reconstructed emission factors may be affected by inaccurate information about the on-road fleet composition, driving conditions different from those considered here, and different contribu-

tions of non-traffic-related sources of sulfate and PM<sub>2.5</sub> at the two roadway sites.

Overall, these results demonstrate that Eq. (1) can be used to derive roadway-based emission factors for several PM species that are at a minimum within reasonable agreement with those obtained in roadway tunnel measurements.

### 3.2. Comparison of roadway and reconstructed tunnel emission factors for organic tracers

Table 2 shows average emission factors of PAHs, hopanes and steranes quantified from the analyses of the PM samples collected at the I-710 freeway and the CA-110 highway. The emission factors of light molecular weight (MW) PAHs such as

Table 2

Emission factors of PAHs, hopanes and steranes (expressed in  $\mu\text{g kg}^{-1}$  of fuel burned) analyzed in  $\text{PM}_{2.5}$  samples collected at the CA-110 and the I-710 sites

	CA-110		I-710	
	Average	SD	Average	SD
PAHs ( $\mu\text{g kg}^{-1}$ )				
Fluoranthene	2.86	0.46	16.29	2.81
Pyrene	3.3	0.54	23.21	4.17
Benzo( <i>ghi</i> )fluoranthene	0.68	0.16	16.45	3.83
Benzo( <i>x</i> )anthracene	0.43	0.17	12.24	2.85
Chrysene	2.73	0.41	9.13	2.63
Benzo ( $\beta + k$ )fluoranthene	1.29	0.35	9.05	1.81
Benzo( <i>j</i> )fluoranthene			2.53	0.51
Benzo( <i>e</i> )pyrene	0.76	0.25	7.46	2.31
Benzo( <i>x</i> )pyrene	0.4	0.18	3.52	1.84
Perylene	0.07	0.03	1.82	0.55
Indeno(cd)Pyrene	2.93	0.45	5.99	2.08
Benzo( <i>ghi</i> )perylene	12.3	2.34	13.61	4.29
Coronene	6.21	1.22	7.09	1.42
Hopanes and steranes ( $\mu\text{g kg}^{-1}$ )				
22,29,30-Trisnorhopane	1.5	0.48	7.71	2.09
22,29,30-Trisnorneohopane	2.42	0.74		
17 $\alpha$ (H)-21 $\beta$ (H)-29-norhopane	4.85	1.87	20.14	5.26
18 $\alpha$ (H)-29-norneohopane	1.78	0.76		
17 $\alpha$ (H)-21 $\beta$ (H)-hopane	4.52	2.05	14.14	4.53
22S, 17 $\alpha$ (H),21 $\beta$ (H)-homohopane	2.66	1.08	6.36	2.17
22R, 17 $\alpha$ (H),21 $\beta$ (H)-homohopane	2.14	0.92	4.92	2.06
22S, 17 $\alpha$ (H),21 $\beta$ (H)-bishomohopane	1.15	0.39	3.53	1.81
22R, 17 $\alpha$ (H),21 $\beta$ (H)-bishomohopane	1.17	0.5	2.6	0.78
22S, 17 $\alpha$ (H),21 $\beta$ (H)-trishomohopane	0.99	0.3		
22R, 17 $\alpha$ (H),21 $\beta$ (H)-trishomohopane	0.69	0.27		
20R + S, $\alpha\beta\beta$ -cholestane	0.33	0.09		
20R, $\alpha\alpha\alpha$ -cholestane	1.76	0.52	6.58	2.7
20R + S, $\alpha\beta\beta$ -ergostane	0.02	0.01		
20(R + S), $\alpha\beta\beta$ -sitostane	2.72	0.78	11.6	5.07

fluoranthene, pyrene and benzo-(*ghi*)-fluoranthene, estimated at the I-710 site were substantially higher than those at the CA-110 site. Emission factors for heavier MW PAHs, such as benzo-(*ghi*)-perylene and coronene, however, were comparable at the two roadways, despite of the much higher diesel truck fractions at the I-710 site. The elevated PAHs emissions observed at the CA-110 site can be attributed to the fact that the lube oil in gasoline vehicles absorbs and concentrates heavy MW PAHs that are formed during combustion and, as a result, the PAHs associated with this class of vehicles were at least in part released in the atmosphere as a component of unburned lubrication oil. In contrast, the PAH profile of diesel vehicles is similar to the PAH content of their fuel (Zielinska et al., 2004).

The emission factor profiles for hopanes and steranes, considered to be reliable organic tracers

for diesel and gasoline combustion and mostly found in engine lubricating oils (Rogge et al., 1993; Cass, 1998), at the two roadways was quite similar, with the values at the I-710 site being higher by approximately 3–4-fold compared to those at the CA-110 site. Our results are consistent with those obtained by Phuleria et al. (2006) and Schauer et al. (1999, 2002), which indicated that light MW PAHs are predominantly emitted by diesel vehicles, while heavy MW PAHs are released by both gasoline and diesel cars/trucks. Furthermore, Phuleria et al. (2006) demonstrated that the emission factors of hopanes and steranes from LDVs are an order of magnitude lower than those from HDV, which further validates the findings of this study, considering the average 20% fraction of HDV on the I-710 site.

Fig. 2 presents a comparison between the PAHs emission factors ( $E_{\text{PAH}}$ ) estimated at the I-710

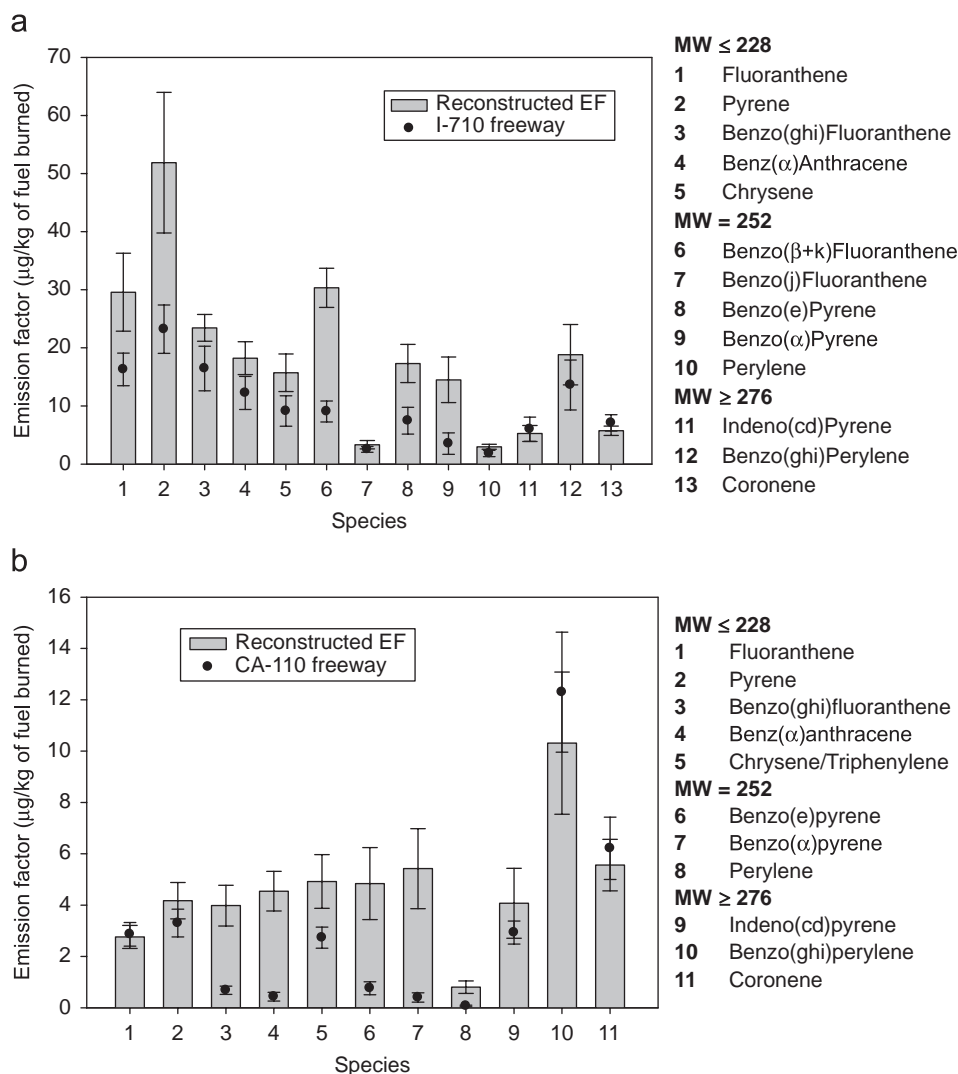


Fig. 2. Comparison among the emission factors of PAHs reconstructed from tunnel measurements and those estimated at the I-710 freeway (a) and at the CA-110 highway (b). All values are expressed in  $\mu\text{g kg}^{-1}$  of fuel burned.

freeway (2a) and at the CA-110 highway (2b), and the correspondent reconstructed values ( $E_{\text{PAH, rec}}$ ) obtained from Caldecott tunnel data (Phuleria et al., 2006) using Eq. (2) (error bars represent the standard deviation).  $E_{\text{PAH}}$  and  $E_{\text{PAH, rec}}$  for high MW PAHs, such as indeno-(cd)-pyrene and coronene, are in very good agreement, with an estimated/reconstructed emission factor ratio ( $E_{\text{p}}/E_{\text{p, rec}}$ ) of 0.90 at the I-710 site and 1.08 at the CA-110 site, for the sum of PAHs with  $\text{MW} \geq 276$ . This agreement suggests that: (a) speciated chemical data collected near roadways can be used to predict reliable emission factors of high MW PAHs at other locations characterized by a similar mix of on-road

motor vehicles and engine operating conditions; and (b) roadway emission factors for high MW PAHs can be predicted with a reasonable accuracy by knowing the vehicle fleet composition and the vehicle source emission profiles. As for lighter MW PAHs, the estimated roadway emission factors were consistently lower than those reconstructed from tunnel data, with an average  $E_{\text{p}}/E_{\text{p, rec}}$  ratio of 0.49 at the I-710 site and 0.40 at the CA-110 site, for the sum of PAHs with a  $\text{MW} \leq 228$  and  $\text{MW} = 252$ . This is probably because this class of organic compounds has relatively high vapor pressures (Schauer et al., 2003) and, thus, can partition between the gas and the particle phase depending



on ambient temperature (Mader and Pankow, 2002). The relatively low and constant temperatures and decreased dilution conditions in the enclosed confines of the tunnel bore are likely to favor the partitioning of light MW PAH into the particle phase. By contrast, the higher temperature and dilution conditions observed near roadways tend to shift the gas-particle partitioning towards the gaseous phase, thus lowering the particle phase emission factors of these species. The higher PAH ratios in the tunnel may also reflect the higher engine load conditions due to the 4% upward grade, as discussed earlier.

Fig. 3 shows a comparison between the emission factors for hopanes and steranes estimated at the I-710 site (3a) and at the CA-110 site (3b), and those

reconstructed from the correspondent tunnel measurements. Estimated and reconstructed values for most hopanes and steranes were in very good agreement (i.e., within 30% or less), which corroborates the use of these two classes of organic compounds as reliable and stable tracers for vehicle emissions in different environments (Schauer et al., 1996; Cass, 1998). The small differences observed between the  $E_p$  and  $E_{p,rec}$  values may be attributed, at least in part, to uncertainties related to the fleet composition and driving conditions.

Paired Student *t*-tests showed no significant difference between measured and reconstructed emission factors for high MW PAHs, and hopanes and steranes at both the I-710 and the CA-110 sites ( $p < 0.05$  at a 95% confidence interval).

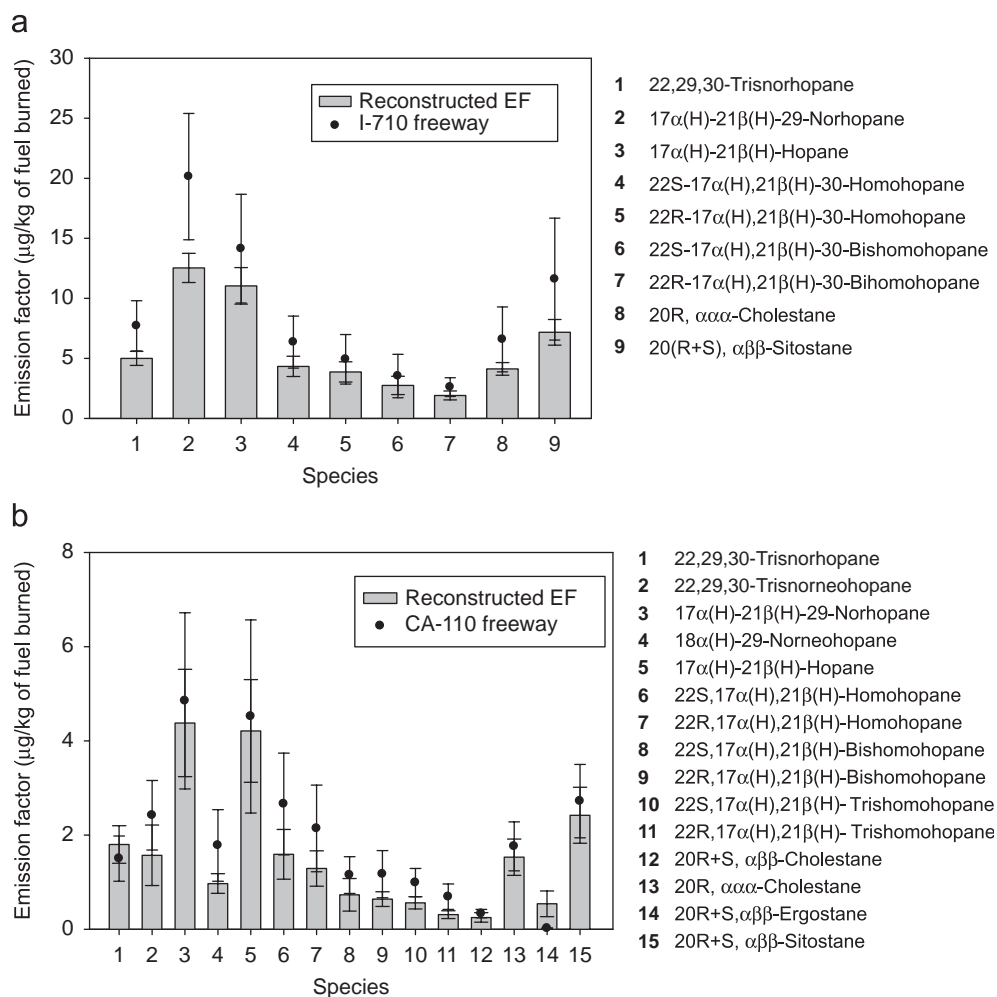


Fig. 3. Comparison among the  $\text{PM}_{2.5}$  emission factors of hopanes and steranes reconstructed from tunnel measurements and those estimated at the I-710 freeway (a) and at the CA-110 highway (b). All values are expressed in  $\mu\text{g kg}^{-1}$  of fuel burned.

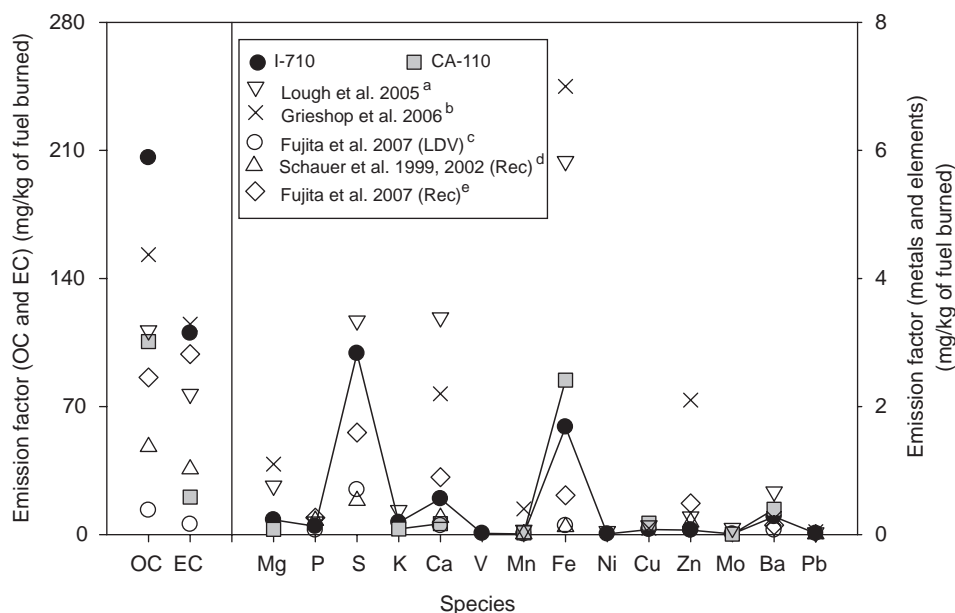
### 3.3. Comparison in emission factors for trace elements, metals, elemental and organic carbon (EC–OC)

Fig. 4 presents a comparison among the emission factors for trace metals ( $E_{\text{metals}}$ ), elements ( $E_{\text{elements}}$ ), and organic and elemental carbon ( $E_{\text{OC}}$  and  $E_{\text{EC}}$ , respectively) obtained in this work at the I-710 and the CA-110 sites (individual average values are shown in Table 1) and those reported in recent roadway tunnel and dynamometer studies by Grieshop et al. (2006), Lough et al. (2005), Fujita et al. (2007) and Schauer et al. (1999, 2002). Grieshop et al. (2006) determined fuel-based emission factors at the Squirrel Hill Tunnel in Pittsburgh, PA, where the HDV fraction ranged from  $3.4 \pm 0.5\%$  during rush hours to  $14.5 \pm 4\%$  early in the morning (to favor a more direct comparison with our data only emission factors corresponding to early morning traffic conditions were considered). Lough et al. (2005) obtained emission rates at two tunnels in Milwaukee, WI, characterized by an HDV fraction between 1.5% and 10% (only data corresponding to

the highest HDV fraction were taken into account in Fig. 4). Emission rates were converted to fuel-based emission factors using the following equation:

$$E_p = ER \times C_f \times D_f, \quad (4)$$

where  $E_p$  is the fuel-based emission factor in PM mass of element/trace metal per kg of fuel burned ( $\text{mg kg}^{-1}$  of fuel burned); ER is the reported emission rate in PM mass of element/trace metal per km driven and per vehicle ( $\text{mg km}^{-1} \text{ vehicle}^{-1}$ );  $C_f$  and  $D_f$  are the average fuel consumption ( $\text{l km}^{-1}$ ) and the fuel density ( $\text{kg l}^{-1}$ ), respectively, reported by Kirchstetter et al. (1999) and weighed by the fraction of gasoline/diesel fuelled vehicles. In a series of chassis dynamometer experiments conducted in the mid-1990s Schauer et al. determined emission rates for two medium-duty-diesel trucks (1999) and eleven gasoline-powered motor vehicles (2002). To facilitate the comparison with our CA-110 and I-710 data, the reported emission rates were converted to fuel-based emission factors (Eq. (4)), and only reconstructed values (Eq. (2)) were then considered in Fig. 4. In that figure,



Note: <sup>a</sup> 2000–2001 study in Howell tunnel (Milwaukee, WI) with 6–10% HDV fraction; <sup>b</sup> 2002 study in the Squirrel Hill Tunnel (Pittsburgh, PA) with 14.5% HDV fraction; <sup>c</sup> Run on unified warm test cycle, 4 LDVs (Model year 1995–1997); <sup>d</sup> Rec (Reconstructed) emission factors based on 2 HDVs (Model year 1995) and 9 LDVs (Model year 1981–1994) tested on FTP cycle; Rec=0.2HDV+0.8LDV; <sup>e</sup> Rec (Reconstructed) emission factors based on unified warm test cycle of 4 LDVs (Model year 1995–1997) and highway test cycle of 15 HDVs (Model year 1985–2001). Rec=0.2HDV+0.8LDV;

Fig. 4. Comparison among  $\text{PM}_{2.5}$  emission factors of organic and elemental carbon (OC and EC, respectively), metals and trace elements from roadway measurements and tunnel and dynamometer studies. All values are expressed in  $\text{mg kg}^{-1}$  of fuel burned.

$E_{p,HDV}$  = emission factor of HDVs as reported by the author, and  $E_{p,LDV}$  = emission factor of LDVs equipped with catalytic converter. Finally, Fujita et al. (2007) ran a set of dynamometer tests on 30 diesel trucks, 57 light-duty gasoline vehicles and 2 light-duty-diesel vehicles (grouped by vehicle weight, model year and mileage category) to assess the sources of uncertainties in quantifying the relative contributions of gasoline and diesel engines' emissions to ambient  $PM_{2.5}$ . Similarly, we converted their reported emission rates to fuel-based emission factors, and considered only (a) the results for low-emitting LDVs in warm starting conditions (i.e., conditions comparable to our field measurements, and (b) the emission factors reconstructed according to Eq. (2) (where  $E_{p,HDV}$  = reported values for HDVs operating on highway driving cycles, and  $E_{p,LDV}$  = data for low-emitting LDVs in warm starting conditions).

Very good agreement among studies was obtained for the species characterized by the lowest emission factors [i.e., phosphorous (P), potassium (K), manganese (Mn), copper (Cu), molybdenum (Mo), lead (Pb) and barium (Ba)], while the largest differences were observed for magnesium (Mg), sulfur (S), calcium (Ca) and, especially, iron (Fe) (Fig. 4). Although, the sum of the emissions of P, V, Ni, Cu, Mo, Ba and Pb does not represent a substantial fraction of the PM mass, most of these species are considered to be important in terms of health effects. For example, Pb was classified by the USEPA as an air toxic, along with Mn, Ni and a few other elements/trace metals. Geller et al. (2006) and Ntziachristos et al. (2007a) have shown that Ba and Cu are found in similar (Ba) or higher (Cu) amounts in gasoline vehicle exhausts, a result that is also corroborated by our own findings shown in Table 1, indicating higher emission factor at the CA-110 site than the I-710 site for these two elements. Pb is emitted from several sources, including fuel and motor oil combustion, brake wear, resuspension of enriched road dust and, in particular, wheel weights which are dropped from vehicle wheels and pulverized by traffic (Lough et al., 2005). Mo is used as a component of automotive catalysts and as an anti-friction additive in lubricating oils (Grieshop et al., 2006) and its emission rates were not significantly elevated relative to background levels. Overall, the considerable contributions of LDVs to the airborne PM concentrations of these species may explain the closer agreement in the emission factors among the various studies, as it

reduces the relevance of the HDV fraction on their overall emissions.

As illustrated in Fig. 4, the highest emission factors were found for Fe, Ca and S, the sum of which typically represents the most substantial portion of the element/trace metals contribution to atmospheric PM (Lough et al., 2005). Along with Mg, Fe and Ca are major components of crustal materials and soil, and their presence in the particulate phase is predominantly attributed to road resuspension (Grieshop et al., 2006). This may explain why the emission factors of Fe, Ca and Mg obtained during the considered tunnel studies were higher than those reported or reconstructed from the cited dynamometer experiments (Fig. 4). Additional important roadway sources for these elements include combustion of motor oil additives for Ca, Mg and S, and the wearing of engines, tires and brakes, and tailpipe emissions (for Fe). S is also produced in great amounts from emissions of sulfur containing fuel (Swietlicki et al., 1996; Kittelson, 1998), the consumption of lubricant oil motor (Geller et al., 2006), and additives such as zinc dithiophosphate (also a substantial source of Zn along with brake- and tire-wear, and tailpipe emissions of motor oil) (Lough et al., 2005). As expected, the emission factor of S at the I-710 site was among the highest because of the higher levels of sulfur in diesel fuel compared to gasoline fuel. The fact that the atmospheric concentrations of Fe, Ca, S and Mg are associated with both traffic and non-traffic sources (e.g., road and soil dust), and that the relative abundances of Mg, Ca and Fe in road dust varies considerably across locations complicates the direct comparison and interpretation of their emission factors and justify the discrepancies among studies observed in Fig. 4. It is also interesting to note that the lowest emission factors for each of the considered element/trace metals were found in the two dynamometer studies, probably because they only include the contribution of motor-vehicles and not the additional effect of resuspension of road dust to the airborne concentrations of these PM species.

The highest emission factors for OC and EC ( $E_{OC}$  and  $E_{EC}$ , respectively) were observed at the I-710 site and in the tunnel experiments by Grieshop et al. (2006) (Fig. 4), and were probably associated with the increased EC emissions from HDVs. The lowest  $E_{OC}$  and  $E_{EC}$  values were obtained for LDVs during the dynamometer tests by Fujita et al. (2007), because LDVs emit in general substantially lower

quantities of OC and EC than HDVs. The somewhat higher  $E_{OC}$  measured at the CA-110 may be related to absorption of vapor-phase organics in the sampling filter during collection (Turpin et al., 2000; Subramanian et al., 2004). Unlike the OC measurements reported by Grieshop et al. (2006), our OC concentrations obtained at the CA-110 and at the I-710 sites were not corrected for this positive artifact and the correspondent  $E_{OC}$  might be slightly overestimated. This positive artifact would be associated with only a portion of our  $PM_{2.5}$  OC emission rate (i.e., the ultrafine range), given that about half of the measured  $PM_{2.5}$  OC was in the accumulation mode (0.18–2.5  $\mu m$ ), which was collected by impaction and should not be affected by positive artifacts induced by adsorption of organic vapors on quartz filters. Nonetheless, the relatively higher OC emission factors of our study suggest that our data may be biased by this phenomenon, and our reported OC emission rates thus need to be interpreted with some caution.

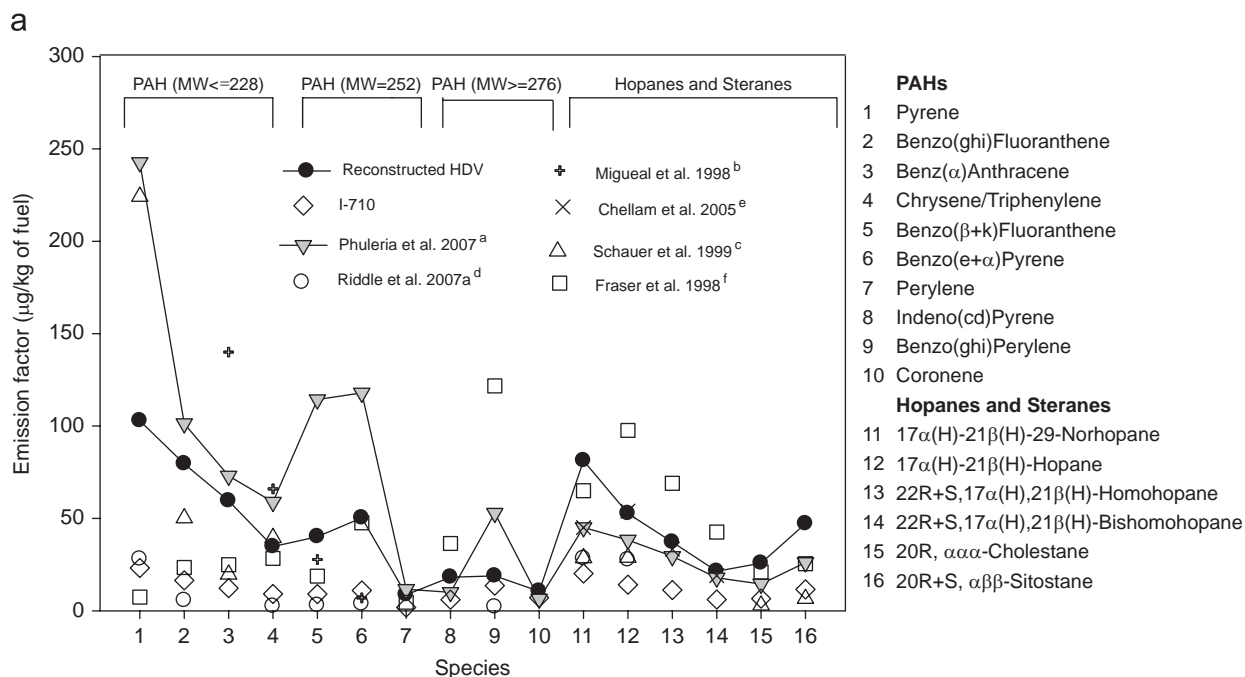
An important factor that may influence the comparison between  $E_{OC}$  and  $E_{EC}$  data from the two dynamometer studies is the analytical method used to determine OC and EC. While Schauer et al. (1999, 2002) employed a NIOSH thermal–optical transmittance (TOT) protocol in a Sunset Laboratory OC/EC analyzer, Fujita et al. (2007) used an IMPROVE thermal–optical reflectance (TOR) method in a DRI carbon analyzer (Chow et al., 2001). Because EC and OC are operationally defined by the analytical method, the use of different thermal evolution protocols can greatly influence the “split” between OC and EC and, thus, the OC/EC ratio (but not the amount of total carbon,  $TC = OC + EC$ , detected). For dynamometer studies, differences in speed and acceleration in the test cycles will lead to different emissions of OC, EC and TC and will certainly impact the EC/OC ratio.

### 3.4. Comparisons in the emission factors of PAHs, hopanes and steranes

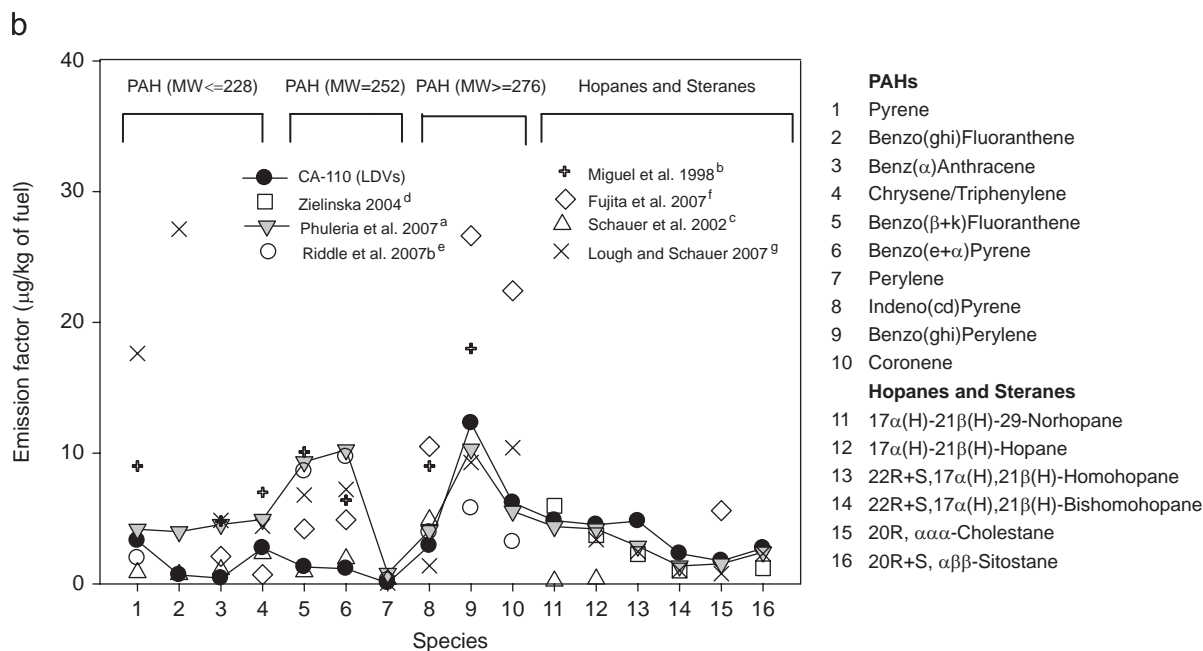
Fig. 5 presents a comparison among emission factors of PAHs, hopanes, and steranes for HDVs (5a) and LDVs (5b), obtained or reconstructed: (a) during our roadway measurements at the I-710 and the CA-110 sites, (b) from recent chassis dynamometer experiments (Schauer et al., 1999, 2002; Zielinska et al., 2004; Riddle et al., 2007a,b; Fujita et al., 2007) and (c) in the course of several

tunnel studies conducted in different parts of the US (Fraser et al., 1998; Miguel et al., 1998; Chellam et al., 2005; Phuleria et al., 2006). All considered PAHs were sorted into three groups based on their MWs (i.e. low  $MW \leq 228$ , medium  $MW = 252$  and high  $MW \geq 276$ ). At the outset of this discussion, we need to emphasize that perfect agreement between our roadway measurements and those reported in previous works should not be expected a priori, mostly because emissions of organics from motor vehicles depend on many factors that are likely to vary substantially among these studies. These include vehicle age and engine load (for chassis dynamometer tests) as well as fleet mix, tunnel up- or downhill grade and ambient temperature conditions (for tunnel and roadway measurements). For example, some of the highest values in Fig. 5a are associated with emissions from old motor vehicles employed by Fraser et al. (1998) and Miguel et al. (1998) in their tunnel studies (conducted in 1993 and 1996, respectively). In this regard, the comparisons presented in this paragraph are mainly intended to provide a range of emissions factors for each organic species and the degree to which the results of the present study lie within that range.

The data shown in Fig. 5a indicate that for all of the organic species, the emission factors determined from our measurements at the I-710 site and those reconstructed for the HDVs contribution to the freeway traffic emissions (Eq. (3)) are well within the range of values reported from previous studies, reflecting the impact of a mixed HDV fleet in real-world freeway environments. In particular, our emission factors of hopanes and steranes are in close agreement with those from the various tunnel and dynamometer studies. For almost all of the organic species, a closer agreement is observed between our data and those from the tunnel measurements compared to the dynamometer tests. This is because the emissions factors based on tunnel studies incorporate the contributions of thousands of vehicles, similarly to our work at the I-710 site, while those derived from dynamometer experiments are representative of a rather limited number of vehicles. In addition to the results of our study, the light- and medium-MW PAHs factors reported by the rest of the studies are higher for HDVs compared to LDVs, probably because the higher engine loads and hotter combustion temperatures in the HDVs engines tend to break down the PAHs with the highest MW (Riddle et al., 2007a). Finally, although coronene has been



Note: <sup>a</sup> 2004 HDV data from the Caldecott tunnel; <sup>b</sup> 1996 HDV data from the Caldecott tunnel; <sup>c</sup> Run on hot-start FTP urban driving cycle, 2 medium HDVs (Model year 1995); <sup>d</sup> Run on 56k pounds load test cycle, 1998 HDV; <sup>e</sup> 2000 Washburn tunnel mixed fleet data in Houston with %HDVs=3.4; <sup>f</sup> 1993 Los Angeles tunnel mixed fleet data with %HDVs=2.7.



Note: <sup>a</sup> 2004 LDV data from the Caldecott tunnel; <sup>b</sup> 1996 LDV data from the Caldecott tunnel; <sup>c</sup> Run on cold-start FTP driving cycle, 9 catalyst-equipped LDVs (Model year 1981-1994); <sup>d</sup> Run on California UDC cycle; 5 catalyst-equipped LDVs (Model year 1993-1996); <sup>e</sup> Run on FTP driving cycle; 6 Three-way catalyst equipped LDVs (Model year 1988-1999); <sup>f</sup> Run on unified warm test cycle; 4 LDVs (Model year 1995-1997); <sup>g</sup> Run on warm start driving cycles; 24 nonsmoker LDVs (Model year 1985-1994).

Fig. 5. Comparison among PM<sub>2.5</sub> emission factors of PAHs, hopanes and steranes for HDVs (a) and LDVs (b) from roadway measurements and tunnel and dynamometer studies. All values are expressed in µg kg<sup>-1</sup> of fuel burned.



proposed as a potential tracer for gasoline motor vehicle exhaust (Schauer et al., 1996; Cass, 1998), this species was detected in substantial amounts (and comparable to those from LDVs) in our study at the I-710 site, as well as in the tunnel studies by Phuleria et al. (2006) and the dynamometer experiments on HDVs operated under low-speed driving conditions by Riddle et al. (2007a) (the latter study proposed the use of large PAHs with MW of 326 and 350 Da as tracers of LDVs emissions instead of coronene).

Fig. 5b shows that for all of the organic species the emission factors determined from our measurements at the CA-110 site are very comparable to those reported from previous studies, especially for PAHs with a MW  $\geq 276$ , hopanes and steranes. The lower emission factors of light- and medium-MW PAHs obtained at the CA-110 site further validates the argument that the higher temperature and dilution conditions in the freeway environment may be shifting the gas-particle equilibrium of these organic compounds towards the gaseous phase (Mader and Pankow, 2002), thus decreasing the correspondent emission factors.

Our results indicate that among all measured PAHs emitted by LDVs those with the highest MW (i.e. indeno-(*cd*)-pyrene, benzo-(*ghi*)-perylene and coronene) are characterized by the highest emission factors. These three PAHs are found both in gasoline and diesel vehicle exhausts, but only in used gasoline vehicle motor oil, and not in fresh or used diesel engine oil (Fujita et al., 2007). The fact that the concentration of these species in gasoline vehicle motor oil increases with the age of the oil, may be the main reason why the magnitude of their emission factors for LDVs varies considerably among studies (Fig. 5b). Emissions of high MW PAH from HDVs are likely to be dominated by “smoking” vehicles characterized by poor combustion conditions. Finally, our results suggest that LDVs exhaust contain a more even distribution by MW of hopanes and steranes than HDVs exhaust, which seems to be dominated by higher amounts of low-MW hopanes.

#### 4. Summary and conclusions

The emission factors of fine particulate matter (PM<sub>2.5</sub>), of several of its organic and inorganic components, and of particle number (PN) were estimated by integrating roadside speciated chemical data and carbon dioxide (CO<sub>2</sub>) concentrations

collected at the CA-110 highway (where only gas-fuelled light-duty vehicles, LDVs, are allowed) and at the I-710 freeway (where about 20% of the traffic is characterized by heavy-duty-diesel vehicles, HDVs). Emission factors at these two roadways were compared to those reconstructed from source emission data obtained at the Caldecott tunnel by Phuleria et al. (2006) and those reported from several other roadway tunnel and chassis dynamometer studies. Very good overall agreement was found between estimated and reconstructed emission factors ( $E_p$  and  $E_{p,rec}$ , respectively) for PM<sub>2.5</sub> mass, PN, elemental carbon (EC), sulfate (S), high MW polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes. The fact that our  $E_p$  and  $E_{p,rec}$  values for almost all non-labile particle species agree within 30% or less is encouraging in using roadway-based emission factors as a reliable proxy of vehicle exhaust characterization. Very good agreement among studies was obtained for phosphorous (P), potassium (K), manganese (Mn), copper (Cu), molybdenum (Mo), lead (Pb) and barium (Ba), while the largest differences were observed for magnesium (Mg), sulfur (S), calcium (Ca) and, especially, iron (Fe), probably because the atmospheric concentrations of these latter metals/trace elements are associated with both traffic and non-traffic sources, and the relative abundances of Mg, Ca and Fe in road dust varies considerably across locations. Highest and lowest emission factors of OC and EC were associated with HDVs and LDVs, respectively. For PAHs, hopanes and steranes the emission factors determined from our roadway measurements were well within the values reported in the literature from tunnel and dynamometer studies, which provides further corroboration to our results. The ability to determine reliable roadway-based  $E_p$  and  $E_{p,rec}$  data for any particulate species could be further improved if more accurate information about the fleet composition and the total carbon content in motor-vehicle emissions were available. Results similar to those obtained herein could be used in epidemiological studies to assess human exposure to PM and its components both inside vehicles and in the immediate proximity of roadways.

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## Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2007.12.039](https://doi.org/10.1016/j.atmosenv.2007.12.039).

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