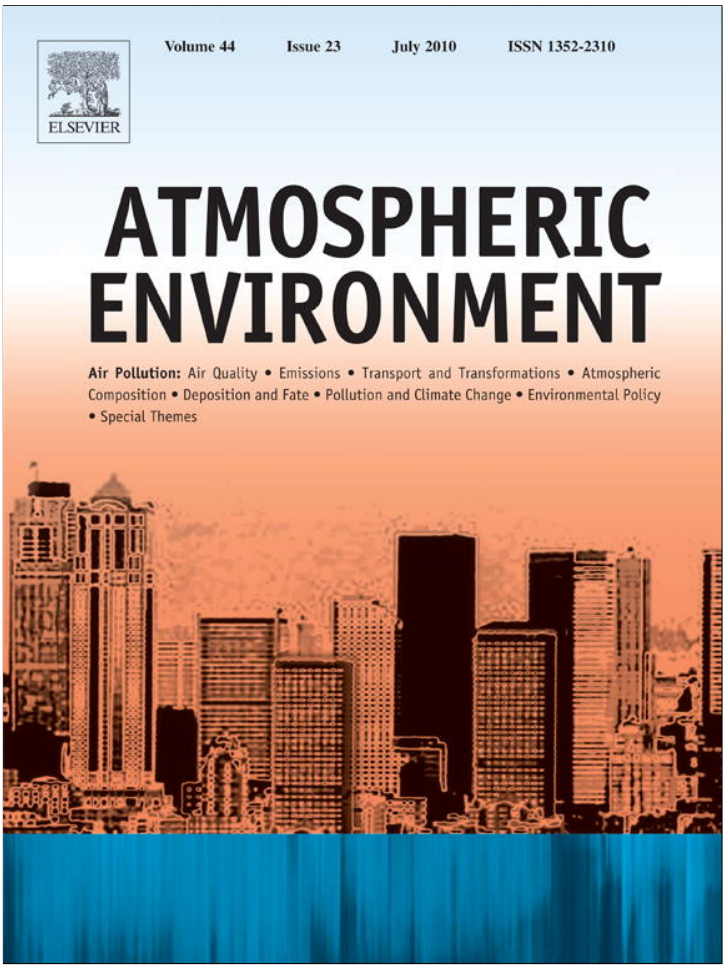

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Characterization of carbon fractions for atmospheric fine particles and nanoparticles in a highway tunnel

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ABSTRACT

Fine particles ($PM_{2.5}$) and nanoparticles ($PM_{0.1}$) were sampled using Dichotomous sampler and MOUDI, respectively, in Xueshan Tunnel, Taiwan. Eight carbon fractions were analyzed using IMPROVE thermal-optical reflectance (TOR) method. The concentrations of different temperature carbon fractions (OC1–OC4, EC1–EC3) in both $PM_{2.5}$ and $PM_{0.1}$ were measured and the correlations between OC and EC were discussed. Results showed that the ratios of OC/EC were 1.26 and 0.67 for $PM_{2.5}$ and $PM_{0.1}$, respectively. The concentration of EC1 was found to be more abundant than other elemental carbon fractions in $PM_{2.5}$, while the most abundant EC fraction in $PM_{0.1}$ was found to be EC2. The variation of contributions for elemental carbon fractions was different among $PM_{2.5}$ and $PM_{0.1}$ samples, which was partly owing to the metal catalysts for soot oxidation. The correlations between char-EC and soot-EC showed that char-EC dominated EC in $PM_{2.5}$ while soot-EC dominated EC in $PM_{0.1}$. Using eight individual carbon fractions, the gasoline and diesel source profiles of $PM_{0.1}$ and $PM_{2.5}$ were extracted and analyzed with the positive matrix factorization (PMF) method.

1. Introduction

Carbonaceous aerosol, including elemental carbon (EC, a chemical structure similar to impure graphite) and organic carbon (OC, a large variety of organic compounds) (Seinfeld and Pandis, 1998), are important components of the atmospheric aerosol due to its impacts on global climate, health effects and pollution in environment. Many studies focused on carbonaceous aerosol in recent years (e.g. IPCC, 2001; Ye et al., 2003; Cao et al., 2004, 2005; Han et al., 2008; Zhang et al., 2007). The methods for the determination of OC and EC have been introduced and developed (Novakov, 1981; Chow et al., 1993, 2001; Fung et al., 2002; Cachier et al., 1989a; Hitzenberger et al., 1996; Birch and Cary, 1996; Lavanchy et al., 1999; Watson et al., 2005) in which the thermal-optical reflectance (TOR) method has been applied in many studies (e.g. Cao et al., 2003; Chow et al., 1993, 2004a). The differentiation of carbon fractions using the TOR method was reliable and gave relatively clear chemical and physical entities for different carbon parts (Han et al., 2009), although some metal catalysts and ions might decrease the activity energy of soot in the analysis process and some water soluble organic carbon were found not to evolve in OC oxidization steps (Novakov and Corrigan, 1995; Yu et al., 2002).

According to the IMPROVE protocol of the TOR method, eight carbon fractions can be defined (Chow et al., 1993, 2004a) including OC1-OC4, OP and EC1-EC3. EC can be divided further into char-EC (EC1-OP) and soot-EC (EC2 + EC3) (Han et al., 2007). Char-EC, formed at relatively low combustion temperatures, are larger particles. Soot-EC is formed at higher temperatures with tens of nanometers in size in which primary particles cluster together into loose agglomerates. The eight carbon fractions, char-EC and soot-EC have been utilized for the source apportionment of fine particles (Cao et al., 2005, 2006; Ho et al., 2003; Kim et al., 2003, 2004; Han et al., 2009), which indicated they were the effective indicators for source identification. Until now, these studies were mostly conducted for fine particles but not nanoparticles (Shen et al., 2007, 2009; Zhang et al., 2009).

This study investigated the eight carbon fractions in a highway tunnel where gasoline and diesel vehicles are the two most major emission sources. Gasoline and diesel vehicle emissions could be separated with their high carbon fractions concentrations whose

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abundance differs between two sources. The previous research for $PM_{2.5}$ showed that gasoline vehicle emissions have high concentrations of the OC fractions. In contrast, diesel emissions were identified based upon the high concentration of EC because it contained lots of high-temperature component of EC particles (Watson et al., 1994, 2001; Kim et al., 2004). In the studies of PMF factor profiles for $PM_{2.5}$, EC2 was found to be the most abundant carbon constituents for diesel-fueled vehicles, while OC2 and OC3 were the most abundant for gasoline vehicles (Cao et al., 2006; Liu et al., 2006). However, the PMF factor profiles for $PM_{0.1}$ have never been discussed in previous studies and are worth investigating in this study.

At present, the studies for nanoparticles were mainly focused on the quantification of particle number, size distributions and mass concentrations (Kittelson et al., 2004; Westerdahl et al., 2005; Zhu et al., 2007; Knibbs et al., 2009; Kumar et al., 2009; Heikkilä et al., 2009). The results showed nanoparticles were the most dominant in total particle number in many locations. Owing to poor ventilation, exposure concentration of particles is high in the tunnels (Westerdahl et al., 2005; Zhu et al., 2005; Fruin et al., 2008; Chen et al., 2010a, 2010b). Many previous studies of carbonaceous components in the tunnels have been conducted (Fraser et al., 1998; Ma et al., 2004; Geller et al., 2005; Huang et al., 2006; Chiang and Huang, 2009; Chen et al., 2010a, 2010b), which reported that OC and EC were the major constituent species of particles emitted from gasoline and diesel vehicles. Nonetheless, the characteristics of the eight carbon fractions, char-EC and soot-EC for nanoparticles in the tunnels environment have rarely been reported. Here we presented the measured results for both fine particles and nanoparticles in Xueshan tunnel, Taiwan. The purposes of the study are (1) to obtain the profile of eight carbon fractions for both fine particles and nanoparticles, (2) to discuss the relationships between OC and EC, char-EC and soot-EC, and (3) to characterize the source apportionments of carbonaceous fractions for fine and nanoparticles in the tunnel.

2. Materials and methods

2.1. Sample collection

The sampling site is located in Xueshan Tunnel, which is the longest tunnel with 12.9 km in Taiwan. Traffic emissions are the major sources in the tunnel because of poor ventilation. Dichotomous samplers (Model SA-241, Andersen Inc., Georgia, USA) were used to collect $PM_{2.5}$ samples (fine particles, aerodynamic diameter $dp < 2.5$ μm) and MOUDIs (Model 110, MSP Corp., MN, USA) were used to collect $PM_{0.1}$ samples (nanoparticles, $dp < 0.1$ μm) in the sampling campaigns. The MOUDIs have 10 size stages with the nominal cutoff diameter of 18 (inlet), 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1 and 0.056 μm, respectively (Marple et al., 1991), in which the nozzle plates of the 10th stages were removed so that only $PM_{0.1}$ samples were collected in the after filters. The substrates used in the study were quartz membrane filters (Tissuqartz 2500QAT-UP, 7201 & 7202, Pall Corp., New York, USA). In the present study, both $PM_{2.5}$ and $PM_{0.1}$ were sampled using the quartz behind quartz (QBQ) approach by Dichotomous samplers and MOUDIs with the flow rate of 16.7 and 30 L min^{-1}, respectively (Chen et al., 2010b). The stages 0–9 of the MOUDIs used silicone grease coated foils to reduce particle bounce so that $PM_{0.1}$ samples were obtained by the quartz after filters accurately. PM samples collected by the silicon grease coated foils in stages 1–9 of MOUDI (18–0.1 μm) were analyzed gravimetrically but not chemically because of interference of grease coating. The average mass concentration of PM_{10} and $PM_{2.5}$ concentrations determined by the MOUDIs were shown to be in agreement with those of the Dichot with a relative deviation of <20% (Chen et al., 2010b).

All quartz filters were pre-heated at 900 °C for 3 h and then stored in aluminum foils before sampling. After sampling, the filters were stored immediately in a cooler packed with ice cubes and transported to the laboratory in 30 min. The samples were then stored in a freezer at −18 °C until OC/EC was analyzed in less than 3 days. The samples for this study were collected in nine sampling campaigns from October 2008 to July 2009, each lasted for 3–6.5 h.

2.2. Carbonaceous aerosol measurement

All the loaded filters for $PM_{2.5}$ and $PM_{0.1}$ were analyzed for OC and EC using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). A punch from the quartz filter was analyzed for three elemental carbon fractions and four organic carbon fractions following the IMPROVE (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow et al., 1993, 2001; Fung et al., 2002; Cao et al., 2003). The method produced data for four OC fractions (OC1, OC2, OC3, and OC4 in a helium atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, respectively), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in a 2% oxygen/98% helium atmosphere at 580 °C, 740 °C, and 840 °C, respectively). The IMPROVE protocol defined OC as OC1 + OC2 + OC3 + OC4 + OP and EC as EC1 + EC2 + EC3-OP. The analyzer was calibrated with known quantities of CH_4 every day. Replicate analyses were performed once per ten samples. Blank sample was also analyzed and the sample results were corrected by the blank sample concentration.

3. Results and discussion

3.1. Concentrations of eight carbon fractions, char-EC and soot-EC for $PM_{2.5}$ and $PM_{0.1}$

As shown in Table 1, the average OC and EC concentrations for $PM_{2.5}$ were 23.9 ± 8.7 and 18.9 ± 5.4 μg m^{-3}, while those of $PM_{0.1}$ were 4.7 ± 2.7 and 7.0 ± 3.6 μg m^{-3}, respectively. The four OC and three EC fractions concentrations for $PM_{2.5}$ were ranked in the following order: OC1 (8.0 ± 2.2 μg m^{-3}) > OC2 (6.1 ± 2.0 μg m^{-3}) > OC3 (3.5 ± 1.4 μg m^{-3}) > OC4 (2.2 ± 0.3 μg m^{-3}) and EC1 (22.2 ± 7.7 μg m^{-3}) > EC2 (0.8 ± 0.6 μg m^{-3}) > EC3 (0 μg m^{-3}), respectively. The ranking for $PM_{0.1}$ was: OC2 (1.7 ± 0.7 μg m^{-3}) > OC1 (1.1 ± 0.9 μg m^{-3}) > OC3 (0.9 ± 0.5 μg m^{-3}) > OC4 (0.3 ± 0.2 μg m^{-3}) and EC2 (6.0 ± 2.2 μg m^{-3}) > EC1 (1.6 ± 1.5 μg m^{-3}) > EC3 (0.0 ± 0.1 μg m^{-3}), respectively. The levels of OC1, OC2, OC3 and OC4 were higher in $PM_{2.5}$ than those in $PM_{0.1}$. The mean concentrations of OP were 4.1 μg m^{-3} and 0.7 μg m^{-3} for $PM_{2.5}$ and $PM_{0.1}$, respectively. The concentration of EC1 was higher than any other elemental carbon fractions in $PM_{2.5}$, while EC2 was the highest in $PM_{0.1}$. EC3 was almost under the method detection limit in both $PM_{2.5}$ and $PM_{0.1}$ (Fig. 1). OC of $PM_{0.1}$ accounted for 20% of $PM_{2.5}$ OC, whereas EC of $PM_{0.1}$ accounted for 37% of $PM_{2.5}$ EC, which reflected the presence of richer EC content in nanoparticles.

Table 2 shows the comparison of the average OC and EC concentrations of $PM_{2.5}$ and $PM_{0.1}$ from Xueshan Tunnel with data published in the literature from other sites. $PM_{2.5}$ OC concentrations were found to be comparable with $PM_{0.1}$ at Buk-Ak tunnel Korea, roughly twice those of $PM_{2.5}$ from Chung-Liao tunnel, $PM_{1.6}$ from Van Nuys Tunnel and PM_{10} from Caldecott Tunnel, but much lower than those of $PM_{2.5}$ at Zhujiang tunnel. For EC of $PM_{2.5}$, the concentrations were comparable to those of Caldecott Tunnel and Chung-Liao tunnel, twice those of Van Nuys Tunnel, but only one fourth to fifth of those from Zhujiang tunnel. The OC concentrations of $PM_{0.1}$ in the present study were much lower, only half to one tenth of those at other tunnels. The average $PM_{0.1}$ EC levels were similar to those in Van Nuys Tunnel, but much lower than those of other tunnels shown in Table 2 and less than one tenth of that at Buk-Ak

Table 1
Mass concentrations of 8 carbon fractions and the ratio of OC/EC in $PM_{2.5}$ and $PM_{0.1}$.

Mean Conc. (μgm^{-3}) and Stdev.		OC1	OC2	OC3	OC4	OP	EC1	EC2	EC3	OC	EC	OC/EC
$PM_{2.5}$	Ave.	8.0	6.1	3.5	2.2	4.1	22.2	0.8	*	23.9	18.9	1.26
	Stdev.	2.2	2.0	1.4	0.3	3.0	7.7	0.6	*	8.7	5.4	
$PM_{0.1}$	Ave.	1.1	1.7	0.9	0.3	0.7	1.6	6.0	*	4.7	6.9	0.68
	Stdev.	0.9	0.7	0.5	0.2	0.3	1.5	2.2	0.1	2.7	3.6	

*under the method detection limit.

tunnel in Korea and Zhujiang tunnel in China. For the urban areas in Taiwan, previous study showed that concentrations of OC and EC in $PM_{2.5}$ were 17.0 and 10.4 $\mu g\ m^{-3}$ (Tsai and Chen, 2006) and 11.6 and 4.0 $\mu g\ m^{-3}$ (Lin and Tai, 2001), respectively. The comparison showed that $PM_{2.5}$ OC and EC concentrations in Xueshan tunnel were higher than other urban environments in Taiwan.

The concentrations of char-EC and soot-EC in $PM_{2.5}$ were 18.1 and 0.8 $\mu g\ m^{-3}$, and those for $PM_{0.1}$ were 0.9 and 6.1 $\mu g\ m^{-3}$, respectively. Higher concentrations were found for char-EC in $PM_{2.5}$ and soot-EC in $PM_{0.1}$, which accounted for 96% and 87% of the total EC from $PM_{2.5}$ and $PM_{0.1}$, respectively. The results were consistent with the results of Han et al. (2007) who found more abundant char-EC for fine samples and soot-EC for ultrafine samples. Previous study reported the average char-EC and soot-EC concentrations of $PM_{2.5}$ for fourteen cities in China were 8.7 and 1.26 $\mu g\ m^{-3}$ in winter; 2.4 and 1.21 $\mu g\ m^{-3}$ in summer, respectively (Han et al., 2009). The variation in char-EC and soot-EC was mainly attributed to the different fuel consumptions between winter and summer (Han et al., 2009). In comparison, the present study showed that part of soot-EC from $PM_{0.1}$ was evolved as the char-EC in $PM_{2.5}$ owing to the catalytic activity of abundant metals in tunnel. Details will be discussed in the following section.

3.2. The 8 carbon fraction contributions to total carbon for $PM_{2.5}$ and $PM_{0.1}$

There were distinct differences among $PM_{2.5}$ and $PM_{0.1}$ samples for carbon fraction contributions (Fig. 2). The contributions of four organic carbon fractions (OC1, OC2, OC3 and OC4) to TC in $PM_{2.5}$ and $PM_{0.1}$ were comparable, which ranged from 4.6% to 15.2% in $PM_{2.5}$ and 2.9% to 14.0% in $PM_{0.1}$, respectively. EC1 accounted for 49% of TC in $PM_{2.5}$ samples, which is higher than that in $PM_{0.1}$ samples (13.3%). EC2 contributed 1.7% for TC in $PM_{2.5}$ samples, while much higher contribution (48.5%) was found in $PM_{0.1}$. The variation of contributions for EC1 and EC2 in $PM_{2.5}$ and $PM_{0.1}$ was distinct, which was partly owing to the catalytic activity of some metals. In the tunnel microenvironment, the emission and the re-suspension from road traffic was found to be the sources of metallic elements in the particles (Sternbeck et al., 2002) which promote combustion activity of particles. For example, Cu–Ce–Al mixed oxides have been shown to be active for soot oxidation (Wu et al., 2009). Cu–K/ZrO_2 catalyst is able to lower the soot oxidation temperature significantly by almost 200° (Courcot et al., 2009). Alkali-doped FeV/Al_2O_3 systems and MnO_x–CeO_2 mixed oxides were shown to be excellent catalysts for low-temperature soot oxidation (Neri et al., 2003; Tikhomirov et al., 2006). Jiménez et al. (2008) showed the addition of alkali metals (Li, Na, K) over a CaO–MgO mixture generated a significant increase in the catalytic activity for soot combustion. In present study, the mean concentrations of the major metal elements (Na, Mg, Al, K, Ca, Fe and Si) in $PM_{2.5}$ and $PM_{0.1}$ were 5.1 and 2.5 $\mu g\ m^{-3}$, respectively. The concentrations of sub-major metal elements (S, Zn, Ni, Cu, Mn, Sr, Ag, Ba, Pb, V, Cr and Ti) were 1.5 and 0.8 $\mu g\ m^{-3}$ for $PM_{2.5}$ and $PM_{0.1}$, respectively. Concentrations of metals were found to be much higher in $PM_{2.5}$. The abundance of metals in samples can lower the soot oxidation temperature and make high-temperature soot evolved as low-temperature soot in the carbon fraction determination. Therefore, it was reasonable that part of EC2 from $PM_{0.1}$ was converted to EC1 in $PM_{2.5}$ when the catalytic activity was promoted by metals. The investigations of EC reference materials oxidation also showed that activation energy is lower for char samples (more abundant in coarse samples) than that for diesel soot samples (more abundant in ultrafine samples), which resulted in the peaks of EC1 and EC2 for char and diesel soot samples, respectively (Han et al., 2007). The results were consistent with the present study which showed char-EC dominated EC in $PM_{2.5}$ while soot-EC dominated EC in $PM_{0.1}$.

3.3. Relationships between OC and EC, char-EC and soot-EC for $PM_{2.5}$ and $PM_{0.1}$ in tunnel

Correlations between OC, EC, char-EC and soot-EC of $PM_{2.5}$ and $PM_{0.1}$ are shown in Table 3. The char-EC and soot-EC concentrations were not strongly correlated for $PM_{2.5}$ ($r = 0.57$) and $PM_{0.1}$ ($r = 0.19$). However, strong correlation between OC and EC was observed for $PM_{2.5}$ ($r = 0.96$) and $PM_{0.1}$ ($r = 0.90$), which attributed to the common sources of OC and EC. There was a significant correlation between char-EC and EC for $PM_{2.5}$ ($r = 0.99$). Similar correlation was obtained between soot-EC and EC for $PM_{0.1}$ ($r = 0.93$). Considering

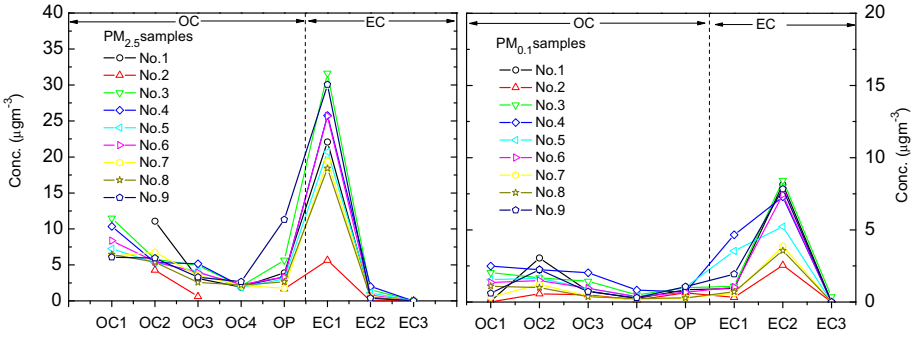

Fig. 1. The concentrations of eight carbon fractions in $PM_{2.5}$ and $PM_{0.1}$.

Table 2
OC and EC concentrations for tunnels at different locations and urban sites in Taiwan and in the world.

Location	Observation Period	Analysis	Particle size	OC, μg m^{-3}	EC, μg m^{-3}	Reference
Xueshan Tunnel Taiwan	Oct.2008–Jul.2009	TOR	$PM_{2.5}$	23.9	18.9	this study
Xueshan Tunnel Taiwan	Oct.2008–Jul.2009	TOR	$PM_{0.1}$	4.7	7.0	this study
Buk-Ak tunnel Korea	Oct.2000	TOR	$PM_{0.1}$	21.9	103.0	Ma et al., 2004
Caldecott Tunnel California	Aug.2004–Sep.2005	TOT	PM_{10}	9.9–17.6	20.5–33.4	Geller et al., 2005
Zhujiang tunnel China	Sep.2004	TOT	$PM_{2.5}$	53.0	94.0	Huang et al., 2006
Chung-Liao tunnel Taiwan	May–Jul.2005	Elemental analyzer	$PM_{2.5}$	10.0 ± 6.3	20.0 ± 7.6	Chiang and Huang, 2009
Van Nuys, Tunnel Los Angeles	1993	TOM	$PM_{1.6}$	15.5 ± 1.4	11.1 ± 1.01	Fraser et al., 1998
Mixed urban, Kaohsiung	Dec.2002–Jan.2003	Elemental analyzer	$PM_{2.5}$	17.0	10.4	Tsai and Chen, 2006
Urban, Kaohsiung	Nov.1998-Apr.1999	Elemental analyzer	$PM_{2.5}$	11.6	4.0	Lin and Tai, 2001

that char-EC dominates EC in $PM_{2.5}$ and soot-EC dominates EC in $PM_{0.1}$, it can be inferred that EC concentration is mainly dominated by char-EC concentration in fine particles while EC is mainly dominated by soot-EC concentration in nanoparticles.

In this study, the ratios of the OC/EC were 1.26 and 0.67 for $PM_{2.5}$ and $PM_{0.1}$, respectively. The previous study reported that OC/EC ratio was 0.56 for fine particles in the tunnel samples (Huang et al., 2006), which was lower than the present study. But the ratios in $PM_{0.1}$ were also compared to those reported for diesel vehicles (0.28–0.92) (Allen et al., 2001). The results indicated the carbon components in nanoparticles mainly came from diesel vehicle emission. Tunnel samples represented fresh emissions from vehicles with lower average OC/EC ratio, while the ambient samples indicated secondary or extra emissions with higher average OC/EC ratio except for vehicle exhausts. In this study, we subtracted the VOC from the backup quartz filter to reduce the overestimation of particle OC and the ratios of OC to EC (Chen et al., 2010b). For comparison, the individual OC to EC ratio was more than 2.0 in Xi'an and Hong Kong for $PM_{2.5}$, while it was 2.7 and 9.0 for coal combustion and biomass burning, respectively. (Cao et al., 2005; Ho et al., 2002; Watson et al., 2001; Cachier et al., 1989b). The high OC to EC ratios were owing to the richer OC sources and the formation of the SOA in the atmosphere, which can affect the OC/EC ratio significantly.

Similar to the OC to EC ratio, the ratios of char-EC to soot-EC also differed among different sources. In the present investigation, the ratios of char-EC to soot-EC were 0.15 for $PM_{0.1}$ and about 20.0 for $PM_{2.5}$. That is, distinctly different ratios between fine and nanoparticles were found. In comparison, the ratios were found to be 22.6 for biomass burning, 1.31 for coal combustion, and 0.60 for motor vehicle exhaust (Chow et al., 2004b). Previous research showed the mean char-EC to soot-EC ratios in Xi'an were 11.6 for biomass burning and 1.9 for coal combustion (Cao et al., 2005). Char-EC/soot-EC ratios showed lower values for summer and higher values for winter over China, which was owing to the differences in source contributions between the two seasons (Han et al., 2009). For the present study, the ratios of char-EC to soot-EC were largely influenced by the redistributions of EC1 and EC2 in $PM_{2.5}$ and $PM_{0.1}$ as discussed above.

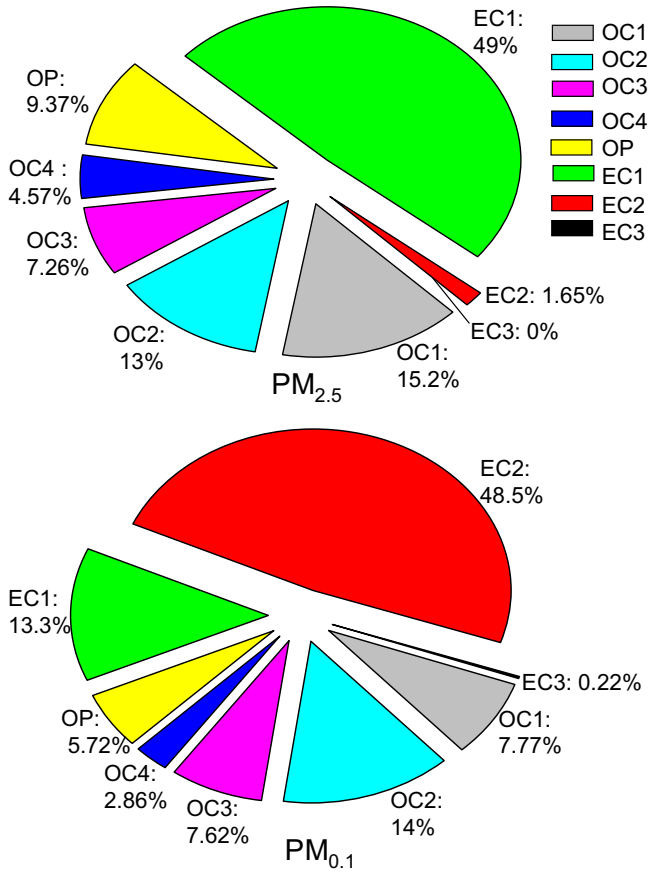

Fig. 2. Percentage of total carbon contributed by eight carbon fractions for $PM_{2.5}$ and $PM_{0.1}$.

3.4. Source identification of carbonaceous fractions in tunnel

PMF is a factor analytic technique that uses non-negativity constraints and allows non-orthogonal factors (Paatero, 1997). PMF1.1 was used for the current analysis (USEPA, 2005). The fractional carbon profiles of $PM_{2.5}$ and $PM_{0.1}$ extracted by the PMF method are shown in Fig. 3. The PMF factor profiles for $PM_{2.5}$ indicated that diesel and gasoline factors had abundant OC1–OC4 and EC1 fractions. The EC2 fraction in the diesel factor was significantly higher than that in gasoline. In comparison, the OC4 and OP fractions in the gasoline factor were more abundant than those in diesel (Fig. 3a). The emissions of the gasoline vehicles had larger amounts of EC2, OC2 and diesel emissions contained higher concentrations of EC2, OC3 and EC3 for $PM_{0.1}$ (Fig. 3b). The results showed there were large amount of lower temperature carbon fractions (OC1–OC4) in $PM_{2.5}$ and higher temperature carbon fractions (EC2) in $PM_{0.1}$.

Table 3
Correlations of OC, EC, char-EC and soot-EC in $PM_{2.5}$ and $PM_{0.1}$.

	OC	EC	char-EC	soot-EC
$PM_{2.5}(n = 9)$				
OC	1.00			
EC	0.96	1.00		
char-EC	0.96	0.99	1.00	
soot-EC	0.56	0.60	0.57	1.00
$PM_{0.1}(n = 9)$				
OC	1.00			
EC	0.90	1.00		
char-EC	0.57	0.52	1.00	
soot-EC	0.78	0.93	0.19	1.00

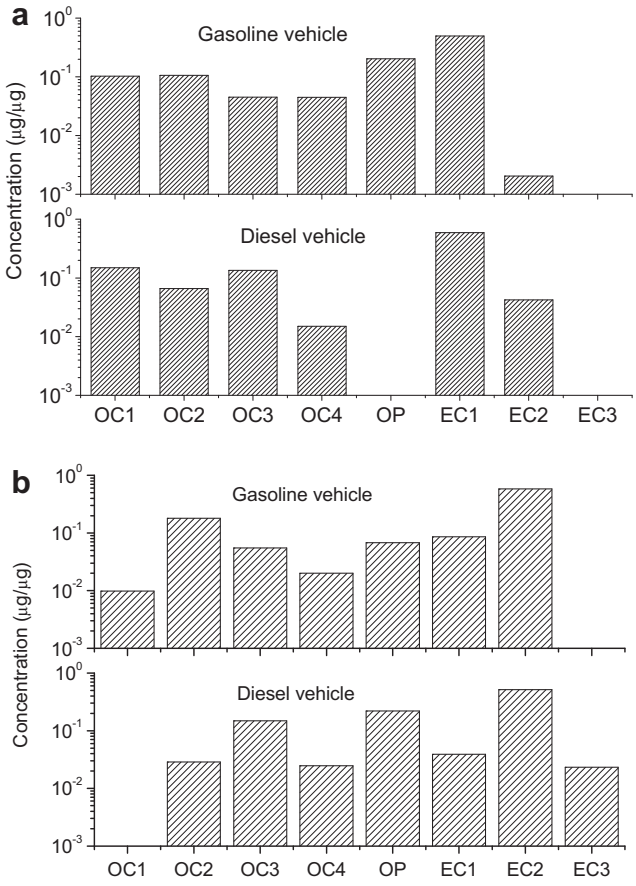

Fig. 3. The diesel and gasoline factor fractional carbon profiles extracted by the PMF method (a) $PM_{2.5}$ and (b) $PM_{0.1}$.

The profiles of OC2 and EC2 fractions in $PM_{2.5}$ for both diesel and gasoline were also in good agreement with the emission profiles obtained by Liu et al. (2006). While the EC2 abundances for $PM_{0.1}$ in both diesel and gasoline profiles were very different from the results of the previous study for fine particles. There was little EC3 in either the diesel or gasoline factor for $PM_{2.5}$ and $PM_{0.1}$.

4. Conclusion

$PM_{2.5}$ and $PM_{0.1}$ were collected and analyzed to determine the eight carbon fractions. The average OC and EC concentrations were 23.9 and 18.9 μg m^{-3} for $PM_{2.5}$, 4.7 and 7.0 μg m^{-3} for $PM_{0.1}$, respectively. The contributions of four organic carbon fractions to TC ranged from 4.6% to 15.2% in $PM_{2.5}$ and 2.9%–14.0% in $PM_{0.1}$, respectively. The concentration of EC1 was higher than any other elemental carbon fractions in $PM_{2.5}$, while EC2 was the dominant fraction in $PM_{0.1}$. The concentrations for char-EC and soot-EC in $PM_{2.5}$ were 18.1 and 0.83 μg m^{-3}, respectively, which those of $PM_{0.1}$ were 0.9 and 6.1 μg m^{-3}, respectively. The char-EC accounted for 96% of the total EC in $PM_{2.5}$ while it was 87% for soot-EC in $PM_{0.1}$. There was a significant correlation between char-EC and EC for $PM_{2.5}$ ($r = 0.99$). Similar correlation was obtained between soot-EC and EC for $PM_{0.1}$ ($r = 0.93$). The results indicated the abundance of soot-EC in $PM_{0.1}$ and char-EC in $PM_{2.5}$ in the tunnel environment. The PMF factor profiles for $PM_{2.5}$ and $PM_{0.1}$ showed both diesel and gasoline factors had abundant EC1 fractions for $PM_{2.5}$ and EC2 for $PM_{0.1}$. In the present study, distinct differences for carbon fraction contributions were found between $PM_{2.5}$ and $PM_{0.1}$. Considering the important catalytic effect of metals on soot oxidation, the influence of catalysis on EC fractions for samples with abundant metals is worth investigating in the future.

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Appendix. Supplementary material

Supplementary material associated with this paper can be found, in the online version, at doi:10.1016/j.atmosenv.2010.04.042.

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