

## Characterization of Roadside Fine Particulate Carbon and its Eight Fractions in Hong Kong

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### Abstract

Simultaneous measurements of PM<sub>2.5</sub> mass, OC and EC and eight carbon fractions were conducted in a roadside microenvironment around Hong Kong for a week in May-June 2002 to obtain the characterization of freshly emitted traffic aerosols. Traffic volume (diesel-powered, liquefied-petroleum gas and gasoline-powered vehicles), meteorological data, and source-dominated samples were also measured. PM<sub>2.5</sub> samples were collected on pre-fired quartz filters with a mini-volume sampler and a portable fine-particle sampler, then analyzed for OC and EC using thermal optical reflectance (TOR) method, following the IMPROVE protocol. High levels of PM<sub>2.5</sub> mass (64.4 µg m<sup>-3</sup>), OC (16.7 µg m<sup>-3</sup>) and EC (17.1 µg m<sup>-3</sup>) observed in the roadside microenvironment were found to be well-correlated with each other. The average OC/EC ratio was 1.0, indicating that OC and EC were both primary pollutants. Marked diurnal PM<sub>2.5</sub> mass OC and EC concentration profiles were observed in accordance with the traffic pattern (especially for diesel vehicles). Average daytime concentrations were 1.3-1.5 times greater than nighttime values. Carbon profiles from source-dominated samples (diesel, LPG and gasoline vehicles) and diurnal variations of eight carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP) demonstrated EC2 and OC2 were the major contributors to the diesel exhaust, and OC3 and OC2 were the larger contributors to the LPG and gasoline exhaust. Thus, carbon fractions derived from the IMPROVE protocol could be used to identify different carbon sources.

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## INTRODUCTION

Motor vehicular emissions are a major source of fine particles in ambient air, especially in urban areas (Harrison et al., 1997; Kerminen et al., 1997; Ruellan et al., 2001; Harley et al., 2005). Road-traffic emission is also an important contributor to the global anthropogenic aerosol burden (Kohler et al., 2001). It has been estimated that in developed countries traffic-related air pollution constitutes more than 50% of the total particulate air pollution (Harrison et al., 1996). Under certain conditions of gross domestic product growth and related transportation activities, the global vehicle population and traveled kilometers are projected to grow extensively in the near future, especially in Asia (OECD, 1995). It is expected that particulate emissions from vehicles will decrease in developed countries and increase in developing countries (APEG, 1999). This stresses the necessity to conduct more studies about motor-vehicular emissions in the developing countries like China, because China is expected to play an ever-increasing role in future global economic activities.

Particulate-phase pollutants emitted by motor vehicles (especially diesel vehicles) consist mostly of carbonaceous aerosol, with its two components elemental carbon (EC, also referred to as black carbon) and organic carbon (OC) (Funasaka et al., 1998). The EC component does not consist of chunks of highly structured pure graphite, but rather is a related, more-complex three-dimensional array of carbon with small amounts of other elements. EC contains a number of crystallites consisting of several carbon layers having the hexagonal structural of graphite (Seinfeld et al., 1998). Ebert (1990) found that fresh soot generated from incomplete combustion of diesel fuel was ~92% carbon, ~6% oxygen, ~1% hydrogen, ~0.5% sulfur, and ~0.3% nitrogen by weight. OC is a complex mixture of hundreds of organic compounds, including numerous unidentified compounds (Watson et al., 2002). Of these organic compounds, species like polycyclic aromatic hydrocarbons (PAHs) are of particular concern, because some PAHs are potent mutagens and carcinogens (Naus et al., 1995). OC and EC in particles also influence urban and regional visibility (Watson et al., 2002), cloud physics and climate forcing (Menon, 2004).

A number of articles and reports have been published regarding the contribution of traffic to OC and EC in Europe and the USA (Kerminen et al., 1997; Miguel et al., 1998; Fraser et al., 1999; Moosmüller et al., 2000; Shi et al., 2000; Kohler et al., 2001; Ruellan et al., 2001). However, only limited studies about roadside carbonaceous aerosols have been conducted in Asia (Bhugwant et al., 2000). Hong Kong is one of the most densely inhabited metropolitan areas in the world, with the majority of the population of seven million crowded into only 15% of an area 1,068 km<sup>2</sup> in size. According to the 2,000 Census, there were 517,000 registered vehicles, about

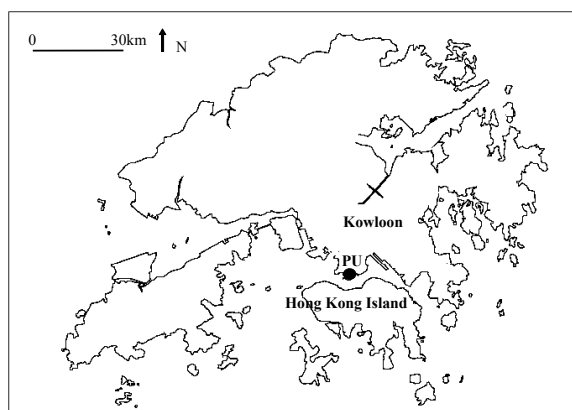
30% of them diesel trucks, crowded into 1,904 km of roads (The Census and Statistics Department of Hong Kong, 2000). Motor vehicles are considered one of the major contributors to air pollution in Hong Kong. Consequently, it is a good place to observe the impact of traffic-related pollutants on the air quality within a large urban area.

An intensive monitoring period was conducted from May to June 2002, focusing on fine particulate matter (PM<sub>2.5</sub>) in a typical roadside location in metropolitan Hong Kong. This roadside category may also be considered a microenvironment, especially for those samples taken in downtown street canyons (Chan et al., 2000). The goal was to characterize the temporal and diurnal variations of PM<sub>2.5</sub>, OC, and EC concentrations at a roadside station influenced by the current on-road fleet of heavy-duty diesel, LPG (liquefied petroleum gas) and light-duty gasoline vehicles. Specific objectives were to: 1) gather a comprehensive set of data on freshly emitted particles and traffic parameters; (2) determine the relationship between the concentrations of eight carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP) and the volume of vehicles plying through the highway. In accomplishing these objectives, the carbon emission profiles for diesel, LPG and gasoline vehicles were also developed.

## **METHODOLOGY**

### ***Sampling location***

The Hong Kong Polytechnic University (PU) is located in Kowloon within a highly urbanized area, and is surrounded by heavily trafficked roads nearby that lead to the Cross Harbor Tunnel (Fig. 1). The sampling station at PU was situated at ground level, and about 1 m away from the main traffic road. The traffic volume was extremely high, with about 170,000 vehicles per day. Therefore, at the sampling site PM<sub>2.5</sub> mass, OC, and EC were expected to reflect primarily the impact of freshly emitted particles from vehicular exhaust. The source-dominated samples were collected, respectively, in a Hong Kong bus depot with a diesel-exhaust microenvironment, a LPG refilling station with a LPG-vehicle exhaust microenvironment, and a car park with a gasoline vehicle-exhaust microenvironment.



**Fig. 1.** Sampling location

### ***Sampling method***

An intensive monitoring program started from May 27, 2002 to June 2, 2002 for daytime (7:00-18:40, local time) and nighttime (19:00-6:40) sampling. Two  $PM_{2.5}$  samples were collected each day using a mini-volume sampler (Airmetrics, USA) at PU station, and operated at a flow rate of  $5 \text{ L/min}^{-1}$ . In order to obtain the detailed information of diurnal variations,  $PM_{2.5}$  samples were collected every two hours on a weekday (May 28) and a weekend day (June 2) using a portable fine particle sampler (Watson et al., 1994). The sampling system consisted of a Teflon-coated  $PM_{2.5}$  cyclone, a Teflon-coated plenum with outlets for each sample, and appropriate pumps and flow controllers. A total of  $113 \text{ L/min}^{-1}$  was drawn through the inlet to be divided among the different sampling substrates. A total of 66 filters were collected during the monitoring program.

Sampling at source-dominated environments with diesel-, gasoline- and-LPG powered vehicles was carried out after intensive monitoring using the portable fine-particle sampler. Two observers during each diurnal sampling hour counted highway traffic manually according to the dominant fuel of each vehicle, diesel, LPG, and gasoline. The vehicle classification followed the specification of the Hong Kong Transport Department in its Annual Traffic Census report in which three vehicle categories are defined. Meteorological data, such as temperature (T) and wind speed (WS) were obtained from Hong Kong King's Park Meteorological Station, approximately 5 km west of the station.

### ***Chemical analysis***

The PM samples were analyzed for OC and EC with a DRI Model 2001 Thermal/Optical Carbon Analyzer according to the IMPROVE protocol using reflectance for pyrolysis correction (Chow et al., 2004; Watson et al., 2005). The protocol heats a  $0.526 \text{ cm}^2$  punch aliquot of a sample quartz filter stepwise at temperatures of  $120^\circ\text{C}$  (OC1),  $250^\circ\text{C}$  (OC2),  $450^\circ\text{C}$  (OC3), and

550°C (OC4) in a non-oxidizing helium (He) atmosphere, and 550°C (EC1), 700°C (EC2), and 800°C (EC3) in an oxidizing atmosphere of 2% oxygen in a balance of helium. The carbon that evolves at each temperature is oxidized to carbon dioxide (CO<sub>2</sub>), then reduced to methane (CH<sub>4</sub>) for quantification with a flame ionization detector. As temperature increases in the inert helium, some of the organic carbon pyrolyzes to black carbon, resulting in darkening of the filter deposit. This darkening is monitored by reflectance of a 633-nm He-Ne laser light. When oxygen is added, the original and pyrolyzed black carbon combusts and the reflectance increases. The amount of carbon measured after oxygen is added until the reflectance achieves its original value is reported as optically-detected pyrolyzed carbon (OP). The eight fractions OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP are reported separately in the data sheet. The IMPROVE protocol defines OC as OC1+OC2+OC3+OC4+OP, and EC as EC1+EC2+EC3-OP (Cao et al., 2004).

### ***Quality assurance and quality control***

For data comparison, a Partisol model 2000 (Rupprecht & Patashnick, USA) low-volume sampler with a 2.5 µm inlet was used for PM<sub>2.5</sub> sampling. The difference in PM<sub>2.5</sub> mass from the mini-volume sampler and portable fine-particle sampler compared to the Partisol 2000 was less than 5%.

PM<sub>2.5</sub> was collected on 47 mm Whatman quartz microfiber filters (QM/A) which were pre-heated before sampling at 900°C for three hours to remove carbonaceous contaminants. After collection, loaded filters were stored in a refrigerator at about 4°C before chemical analysis to prevent the evaporation of volatile components. The PM<sub>2.5</sub> mass was determined gravimetrically using an electronic microbalance with a 1 µg sensitivity (Mettler M3, Switzerland) at the Institute of Earth Environment. Also, field blank filters were collected to subtract the positive artifacts due to adsorption of gas-phase organic components onto the filter during and/or after sampling. However, negative artifacts due to volatilization of particle-phase organics from particle sample were not quantified in this study, due to limited resources.

The carbon analyzer was calibrated with known quantities of CH<sub>4</sub> gases every day. Replicates of analyzed samples were performed at the rate of one per group of 10 samples. Standard samples that had been analyzed by thermal manganese dioxide oxidation (TMO) method (Fung, 1990; Fung et al., 2002) were used as quality control during the analysis. Two standard sucrose spiked filters were used as quality-assurance sample sets. Four field blank filters were also analyzed and the sample results were corrected by the average of the blank concentrations, which were 1.58 and 0.22 µg m<sup>-3</sup> for OC and EC respectively. The detection limits for OC and EC were less than 0.8 and 0.2 µg cm<sup>-2</sup>, respectively, for quartz-fiber filters. The difference between the initial and replicate analyses was smaller than 5% for total carbon (TC), and 10% for OC and EC.

## RESULTS AND DISCUSSION

### *Temporal variations of the concentrations and daytime and nighttime ratio of PM<sub>2.5</sub>, OC, and EC*

PM<sub>2.5</sub>, OC, and EC concentrations, as well as their percentage in total mass between day and night during the intensive monitoring from May 27, 2002 to June 2, 2002, are shown in Table 1. The PM<sub>2.5</sub> concentrations ranged from 39.1 to 91.3  $\mu\text{g m}^{-3}$  with an average of 64.4  $\mu\text{g m}^{-3}$ . The average OC and EC concentrations were 16.7  $\mu\text{g m}^{-3}$  and 17.1  $\mu\text{g m}^{-3}$ . The average PM<sub>2.5</sub>, OC, and EC concentrations were higher than the corresponding ambient concentrations (54.5, 9.6, and 4.7  $\mu\text{g m}^{-3}$ ) (Cao et al., 2003). While the PM<sub>2.5</sub> concentrations in roadside microenvironment was only slightly higher than the ambient level, the roadside OC and EC concentrations were 1.7 and 3.6 times, respectively, higher than those of ambient air. This indicated that motor-vehicular emission is a dominant source of carbonaceous particle pollution in Hong Kong. Compared with roadside observation in Paris, France, the PM<sub>2.5</sub> mass in Hong Kong (64.4  $\mu\text{g m}^{-3}$ ) is higher than that in Paris (39  $\mu\text{g m}^{-3}$ ) (Ruellan et al., 2001). The EC concentration (17.7  $\mu\text{g m}^{-3}$ ) in this study is slightly higher than the black carbon (BC) concentration (measured by an Aethalometer) (13.6  $\mu\text{g m}^{-3}$ ), but the OC concentration (16.7  $\mu\text{g m}^{-3}$ ) in this study was lower than the OC concentration (34.6  $\mu\text{g m}^{-3}$ ) in Paris. To some extent, these differences in OC and EC concentrations are affected by the analytical methods used for the determinations.

Elemental carbon is from primary anthropogenic sources and is not formed by reactions involving gaseous hydrocarbon precursors in the atmosphere. Organic carbon may be emitted directly from sources as primary particles, but secondary organic aerosols can also be formed in the atmosphere from the low vapor pressure products from atmospheric chemical reactions. The ratio of OC to EC concentrations has been used to study emission and transformation characteristics of carbonaceous aerosols. The OC/EC ratios exceeding 2.0 have been used to indicate the presence of secondary organic aerosols (Chow et al., 1996). As shown in Table 1, the OC/EC ratios in this study varied from 0.8 to 1.6, with an overall average of 1.0. Generally speaking, higher OC/EC ratios were observed at night than during the day because fewer diesel vehicles (less commercial activity) passed through the road at night (except on Sunday and holidays). This showed that OC and EC in roadside microenvironment were influenced by the motor-vehicular exhaust; i.e., OC and EC were both primary pollutants. The fact that all the OC/EC ratios were less than 2.0 implied that there was no secondary organic aerosol formation in the roadside station. This observation is expected, as the site was very close to a major road and

**Table 1.** The concentrations of PM<sub>2.5</sub>, OC, and EC and the percentage of TCA<sup>a</sup>, OM<sup>b</sup>, and EC in total mass.

|         | Type  | PM <sub>2.5</sub><br>μg m <sup>-3</sup> | OC<br>μg m <sup>-3</sup> | EC<br>μg m <sup>-3</sup> | OC/EC | TCA<br>% | OM<br>% | EC<br>% |
|---------|-------|---|--------------------------|--------------------------|-------|----------|---------|---------|
| May 27  | Day   | 91.3                                    | 20.2                     | 19.2                     | 1.1   | 56.4     | 35.4    | 21.0    |
|         | Night | 64.8                                    | 16.4                     | 14.6                     | 1.1   | 63.0     | 40.4    | 22.5    |
| May 28  | Day   | 72.9                                    | 17.4                     | 19.0                     | 0.9   | 64.2     | 38.2    | 26.0    |
|         | Night | 50.0                                    | 12.9                     | 11.1                     | 1.2   | 63.4     | 41.2    | 22.2    |
| May 29  | Day   | 60.4                                    | 14.1                     | 17.7                     | 0.8   | 66.7     | 37.3    | 29.4    |
|         | Night | 52.2                                    | 13.1                     | 12.7                     | 1.0   | 64.6     | 40.2    | 24.4    |
| May 30  | Day   | 86.0                                    | 22.4                     | 29.2                     | 0.8   | 75.6     | 41.7    | 33.9    |
|         | Night | 66.7                                    | 18.0                     | 21.8                     | 0.8   | 75.7     | 43.1    | 32.6    |
| May 31  | Day   | 74.6                                    | 20.4                     | 24.0                     | 0.9   | 76.0     | 43.8    | 32.2    |
|         | Night | 57.5                                    | 17.1                     | 18.5                     | 0.9   | 79.9     | 47.7    | 32.2    |
| June 1  | Day   | 84.3                                    | 21.8                     | 23.3                     | 0.9   | 69.1     | 41.4    | 27.7    |
|         | Night | 56.2                                    | 13.9                     | 8.9                      | 1.6   | 55.4     | 39.5    | 15.8    |
| June 2  | Day   | 45.9                                    | 12.8                     | 9.3                      | 1.4   | 65.0     | 44.8    | 20.3    |
|         | Night | 39.1                                    | 10.2                     | 8.5                      | 1.2   | 63.4     | 41.7    | 21.8    |
| Average |       | 64.4                                    | 16.5                     | 17.0                     | 1.0   | 67.0     | 41.2    | 25.9    |

<sup>a</sup> TCA: Total Carbonaceous Aerosol = 1.6\*OC + EC ; <sup>b</sup> OM: organic matter = 1.6\*OC

is consistent with the previous observation in Paris (Ruellan et al., 2001). The primary OC/EC ratio of 1.0 observed in this study is comparable to the OC/EC ratios of 1.1, 1.1, 1.2 and 1.3 as measured at Aveiro, Coimbra, Oporto, and Birmingham, respectively (Castro et al., 1999).

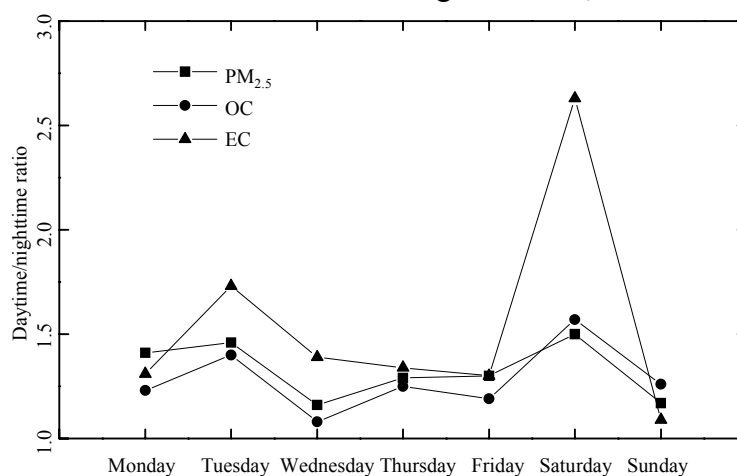
According to White and Roberts (1977), the amount of organic matter (OM) may be determined by multiplying the amount of OC by 1.4. Thus the total carbonaceous aerosol (TCA) in this study was calculated by the sum of organic matter and elemental carbon (OM+EC). The TCA accounts for an averaged 67.0% of PM<sub>2.5</sub> mass loading, while OM and EC account for 41.7% and 26.1%, respectively. For comparison, ambient PM<sub>2.5</sub> in Hong Kong consists of 17.8% OC and 8.7% EC (Cao et al., 2003), corresponding to a TCA of 36.5%. This is about half of the TCA percentage in roadside microenvironment. In other studies, EC accounted for 30-38% of the total mass in fine aerosol at the Caldecott Tunnel (Hering et al., 1984), and 71% of the particulate matter less than 2 μm at a highway tunnel in Osaka (Funasaka et al., 1998). The particles in these tunnels showed great resemblance to those originating from diesel emissions. The EC percentage in total mass in this study (26.1%) is lower than the value in Paris's roadside observation (43%) (Ruellan et al., 2001).

Daytime to nighttime ratios (D/N) of PM<sub>2.5</sub>, OC, and EC during intensive sampling are shown in Fig. 2. PM<sub>2.5</sub>, OC, and EC have higher concentrations in daytime than nighttime (all D/N >1). The average D/N for PM<sub>2.5</sub>, OC and EC are 1.3, 1.3 and 1.5, respectively. Daytime concentration of PM<sub>2.5</sub> ranged from 45.9 to 91.3 μg m<sup>-3</sup> with an average of 73.6 μg m<sup>-3</sup>, while nighttime concentration of PM<sub>2.5</sub> ranged from 39.1 to 66.7 μg m<sup>-3</sup> with an average of 55.2 μg m<sup>-3</sup> (Table 1). Higher OC and EC were also observed in daytime (average OC = 18.7 μg m<sup>-3</sup>; average EC = 20.4

$\mu\text{g m}^{-3}$ ) than in nighttime (average OC =  $14.7 \mu\text{g m}^{-3}$ ; average EC =  $13.8 \mu\text{g m}^{-3}$ ), likely due to commuter and work-related traffic activities (more diesel vehicles) in daytime. The ratios for  $\text{PM}_{2.5}$ , OC, and EC followed similar trends except for a sudden increase on Saturday. Apparently, heavy rain on Saturday night washed out large amounts of EC from the atmosphere, since EC is mostly removed from the atmosphere by wet deposition (Cachier et al., 1996). In the Bhugwant et al. (2000) study, the daytime BC (black carbon) concentrations were two to four times higher than nighttime concentrations underlying the diurnal activity at la Reunion Island in the Southern Indian Ocean. However, Hong Kong is an important commercial center in Asia and human activities continue on well into the night. This led to a smaller difference between day and night time concentrations of  $\text{PM}_{2.5}$ , OC, and EC in Hong Kong.

### *Diurnal variations of the concentrations of $\text{PM}_{2.5}$ , OC, and EC*

In Fig. 3, the diurnal variations of  $\text{PM}_{2.5}$  (two-hour averages) in the weekday and weekend are shown. The concentrations of  $\text{PM}_{2.5}$  on the weekdays were higher than those on the weekend, but all had a pronounced morning peak between 10:00 to 12:00. This might be due to a major increase in the number of diesel vehicles in the morning. However, there was no significant peak



**Fig. 2.** Daytime/nighttime ratio of  $\text{PM}_{2.5}$  mass, OC and EC during the week

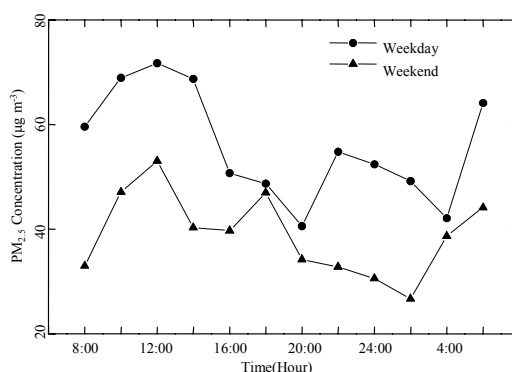
in the evening rush hour on the weekdays. On both weekdays and weekend, the  $\text{PM}_{2.5}$  concentrations were low at night and then gradually increased towards the morning. Obviously, the nighttime  $\text{PM}_{2.5}$  concentrations on weekdays were higher than those on the weekend, since there was less evening traffic. Figs. 4 and 5 show the examples of roadside two-hour average OC and EC concentration profiles during weekday and weekend respectively. Diurnal variations were evident with OC and EC found in the range of  $6.4\text{--}19.7 \mu\text{g m}^{-3}$  and  $5.4\text{--}20.8 \mu\text{g m}^{-3}$ , respectively. As expected, the OC and EC concentrations were at higher levels during the weekday than the weekend, due to the increase in traffic volume and congestion on weekdays. Generally speaking,



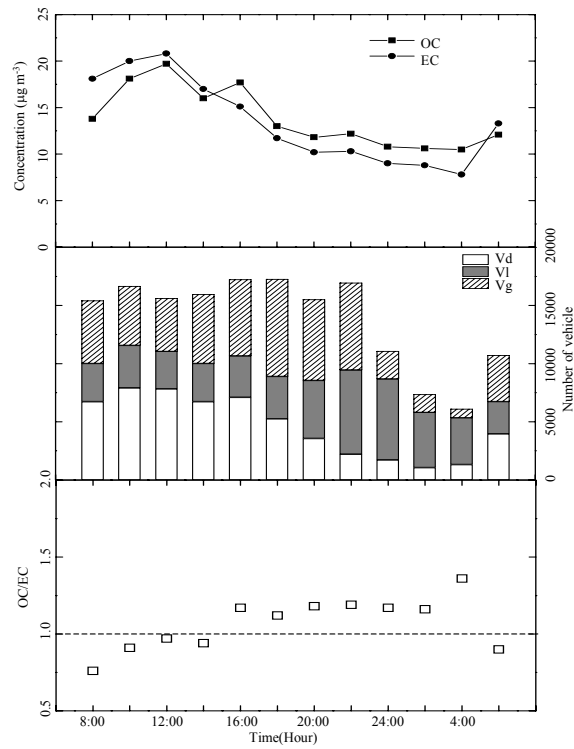
the weekday OC and EC concentrations had similar diurnal patterns. Both showed a large morning peak, then gradually decreased from noon to 6:00 am the next day, except for a small OC peak observed between 16:00-18:00. But on the weekend, there were two OC peaks at 14:00-16:00 and 20:00-22:00, and no obvious EC peak except at dawn on the morning of the following Monday.

To reinforce the hypothesis of a possible relationship between OC and EC concentrations and traffic, shown in Figs. 4 and 5 are the parallel evolution of six parameters: OC, EC, traffic density (vehicles/hour) of diesel, LPG, and gasoline vehicles, and OC/EC ratios for the weekday and weekend. Traffic volume of nine vehicle types (bus, mini-bus, light vehicle, heavy vehicle, van, coach, taxi, private vehicle, and motorcycle) was measured simultaneously during each sample collection. Among the nine types, taxis fell into the LPG vehicle category, private vehicles and motorcycles were classified as gasoline-powered vehicles, and the rest were diesel-powered vehicles. During the daytime, the number of diesel vehicles gradually increased, reaching 40% or more at the peak, and then gradually decreased after 20:00. During the evening peak hour, gasoline vehicles accounted for approximately 50% of the traffic volume due to increasing commuter vehicles. At midnight, LPG taxis became the dominant vehicles on the road (over 50%). In contrast, on weekends, gasoline vehicles were the dominant group, except at midnight. This could be due to a reduction of commercial activities and an increase of outdoor leisure commuters. Of the vehicle types, diesel-engine exhaust is known to be the main source of EC (Watson et al., 1994). Thus, the larger the number of diesel vehicles, the higher the EC concentrations will be.

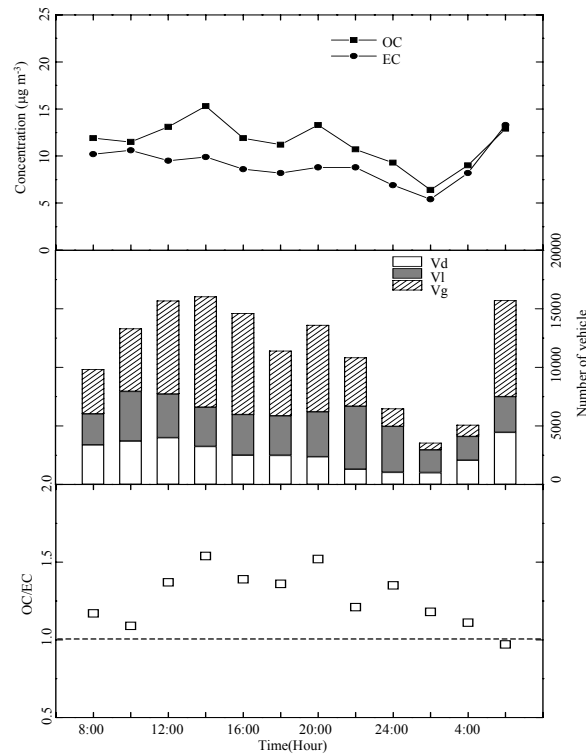
The OC/EC ratios during the weekday and weekend are shown at the bottom part of Figs. 4 and 5. The ratios were below 1.0 from 08:00 to 16:00 on the weekday, at which time the number of diesel vehicles on the road was highest, and more EC was emitted. When gasoline and LPG vehicles were the dominant types of running vehicles, OC/EC ratios were larger than 1.0. During the weekend, nearly all OC/EC ratios were larger than 1.0 except from 06:00 to 08:00 on Monday morning which had an increase of diesel vehicles.



**Fig. 3.** Diurnal variations of PM<sub>2.5</sub> Mass in the weekday and weekend.



**Fig. 4.** Diurnal variations of the concentrations of OC/EC, the number of diesel, gasoline and LPG vehicles, and the ratios of OC/EC during the weekday.



**Fig. 5.** Diurnal variations of the concentrations of OC/EC, the number of diesel, gasoline and LPG vehicles, and the ratios of OC/EC during the weekend.

**Table 2.** Coefficients of correlation among eight carbon fractions, mass, traffic volumes of diesel, gasoline and LPG vehicles, temperature and wind speed.

|                   | OC1   | OC2   | OC3   | OC4   | EC1   | EC2   | EC3   | OP    | OC    | EC    | Mass  | Vd <sup>a</sup> | Vl <sup>b</sup> | Vg <sup>c</sup> | Temp. <sup>d</sup> | WS <sup>e</sup> |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------------|-----------------|-----------------|--------------------|-----------------|
| OC1               |       | *     |       | *     |       |       |       |       | *     | *     |       |                 |                 |                 |                    |                 |
| OC2               | 0.75  |       |       | *     | *     | *     |       | *     | *     | *     | *     | *               |                 |                 |                    | *               |
| OC3               | 0.40  | 0.62  |       |       |       |       |       |       | *     | *     | *     | *               |                 |                 |                    |                 |
| OC4               | 0.80  | 0.87  | 0.55  |       | *     | *     |       |       | *     | *     | *     | *               |                 |                 |                    |                 |
| EC1               | 0.54  | 0.76  | 0.37  | 0.64  |       | *     |       | *     | *     | *     | *     | *               |                 | *               | *                  | *               |
| EC2               | 0.59  | 0.84  | 0.25  | 0.77  | 0.82  |       |       | *     | *     | *     | *     | *               |                 |                 |                    | *               |
| EC3               | 0.24  | 0.03  | 0.20  | 0.12  | 0.13  | -0.08 |       |       |       |       |       |                 |                 |                 |                    |                 |
| OP                | 0.43  | 0.73  | 0.40  | 0.60  | 0.85  | 0.75  | 0.06  |       | *     | *     | *     | *               |                 |                 |                    |                 |
| OC                | 0.78  | 0.94  | 0.61  | 0.88  | 0.81  | 0.83  | 0.18  | 0.76  |       | *     | *     | *               |                 | *               | *                  | *               |
| EC                | 0.64  | 0.88  | 0.41  | 0.78  | 0.91  | 0.96  | 0.03  | 0.80  | 0.86  |       | *     | *               |                 |                 |                    | *               |
| PM <sub>2.5</sub> | 0.48  | 0.76  | 0.48  | 0.64  | 0.73  | 0.77  | -0.11 | 0.76  | 0.70  | 0.82  |       | *               |                 |                 |                    | *               |
| Vd                | 0.61  | 0.85  | 0.37  | 0.65  | 0.89  | 0.88  | 0.04  | 0.77  | 0.83  | 0.94  | 0.79  |                 |                 | *               | *                  | *               |
| Vl                | -0.17 | 0.13  | 0.57  | -0.05 | 0.29  | 0.02  | -0.06 | 0.29  | 0.15  | 0.17  | 0.40  | 0.24            |                 |                 |                    |                 |
| Vg                | 0.35  | 0.48  | 0.45  | 0.32  | 0.64  | 0.48  | 0.21  | 0.46  | 0.63  | 0.55  | 0.50  | 0.65            | 0.41            |                 |                    |                 |
| Temp.             | 0.53  | 0.72  | 0.17  | 0.58  | 0.68  | 0.84  | -0.22 | 0.59  | 0.67  | 0.81  | 0.64  | 0.85            | 0.14            | 0.39            |                    |                 |
| WS                | -0.13 | -0.39 | -0.12 | -0.28 | -0.51 | -0.43 | 0.13  | -0.60 | -0.30 | -0.49 | -0.53 | -0.45           | -0.21           | 0.03            | -0.24              |                 |

\*  $p < 0.001$ ; <sup>a</sup> the volume of diesel vehicles; <sup>b</sup> the volume of LPG vehicles; <sup>c</sup> the volumes of gasoline vehicles; <sup>d</sup> temperature; <sup>e</sup> wind speed

Table 2 shows the relationships between PM<sub>2.5</sub>, EC, OC and the traffic volume of different types of vehicles. The concentrations of PM<sub>2.5</sub>, OC, and EC increased linearly with increases in the traffic volume of diesel vehicles, and significant correlation coefficients were observed:  $r=0.79$  ( $p<0.001$ ),  $r=0.83$  ( $p<0.001$ ) and  $r=0.94$  ( $p<0.001$ ), respectively. The OC concentration varied linearly with the traffic volume of gasoline vehicles ( $r=0.63$ ,  $p<0.001$ ). On the contrary, there was no positive correlation between these concentrations and the number of LPG vehicles.

### ***Characterization of eight carbon fractions in source-dominated samples (diesel, LPG, and gasoline) and diurnal variation of eight fractions***

By using the TOR method, the concentrations of OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP were measured separately in a run by the Thermal/Optical Carbon Analyzer. IMPROVE protocol defines OC as OC1+OC2+OC3+OC4+OP and EC as EC1+EC2+EC3-OP. Carbon abundances in each of these fractions vary with different carbon sources (Ellis and Novakov 1982; Watson et al., 1994). The eight carbon fractions have been used as source markers for carbon apportionment by CMB (chemical mass balance) and PMF (positive matrix factorization) model (Lewtas, 2002). The contents of eight fractions have also been utilized in source profile studies to differentiate gasoline vehicles from diesel vehicles. The eight fractions are also included in the

IMPROVE database and form the basis for calculating the organics and elemental carbon fractions for light extinction used by the U.S. Environmental Protection Agency (USEPA, 2001). Consequently, the eight carbon fractions reported by the IMPROVE method provide a useful tool in identifying particulate carbon sources.

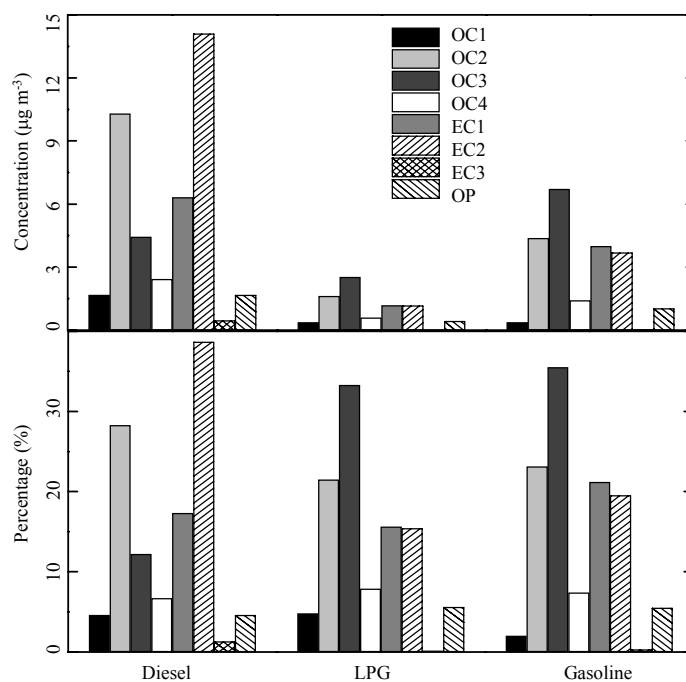
The carbon profiles of eight carbon fractions of source-dominant samples (diesel, LPG and gasoline vehicles) are shown in Fig. 6. EC2 was the major exhaust of diesel vehicles, followed by OC2. EC2 and OC2 accounted for about 38.2% and 26.7% of the TC (the sum of OC and EC), respectively. Gasoline- and LPG-vehicle exhaust had similar carbon profiles; i.e., OC3 was the dominant species, followed by OC2. The percentages of OC3 and OC2 in the TC for LPG vehicles were 33.3% and 21.5%, respectively. The corresponding values for gasoline vehicles were 35.5% and 23.1%, respectively. Our results regarding diesel and gasoline vehicles are identical with previous observations (Watson et al., 1994), where EC2/OC2 were the dominant components of diesel exhaust and OC3/OC2 were the large components of gasoline exhaust.

For comparison, the source-dominated samples were collected for equal amounts (100 units) of diesel, LPG, and gasoline vehicles, respectively. Obviously, the OC concentration in diesel vehicular ( $17.2 \mu\text{g m}^{-3}$ ) exhaust was 3.3 and 1.4 times, respectively, than that in LPG ( $5.2 \mu\text{g m}^{-3}$ ) and gasoline vehicular ( $12.4 \mu\text{g m}^{-3}$ ) exhausts (Fig. 6). And EC in diesel vehicular ( $19.2 \mu\text{g m}^{-3}$ ) exhaust was 7.4 and 2.8 times, respectively, than that in LPG ( $2.5 \mu\text{g m}^{-3}$ ) and gasoline vehicular ( $6.8 \mu\text{g m}^{-3}$ ) exhaust (Fig. 6). Therefore, diesel vehicle was a dominant contributor to ambient EC and OC.

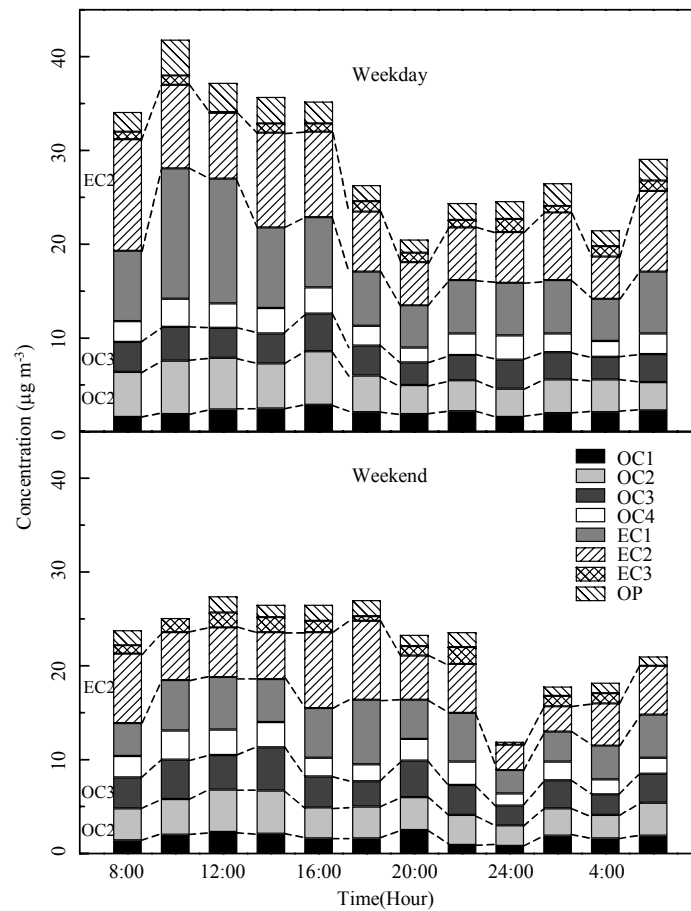
Diurnal variations of OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP are shown in Fig. 7. On weekdays, EC2 was high, from 08:00 to 18:00, due to the large number of diesel vehicles on the highway, ranging from 6,732 to 7,920 during a two-hour period. EC2 decreased from 18:00 to 06:00 with a decrease in the number of diesel vehicles. During 06:00-08:00, EC2 returned to a high level along with an increase of diesel vehicles. OC2 followed a similar trend as EC2 during weekdays. But the difference between daytime and nighttime OC3 was smaller than that observed for EC2, probably because diesel, LPG and gasoline vehicles all contributed to the ambient OC3 concentration, as seen in Fig. 6. On the weekend, the concentrations of EC2, OC2 and OC3 were lower than the corresponding values during the weekday. The daytime EC2 level was higher than that during the night because of the higher proportion of diesels in the traffic count. This implies that EC2 may be used as an indicator of diesel exhaust and that diurnal EC2 variations show the impact of diesels with consistent characteristics. The diurnal variation of OC2 was close to the variation of EC2. Two OC3 peaks had been observed 14:00-16:00 and 20:00-22:00 resulting from a high proportion of LPG and gasoline vehicles on the highway.

Table 2 shows the correlation coefficients among concentrations of the eight carbon fractions, traffic volumes of diesel, gasoline and LPG vehicles, and other meteorological data (temperature and wind speed). The concentration of OC1, OC2, OC4, EC1, EC2, OP and mass increased with

the diesel traffic volume and significant correlation coefficients were observed:  $r$  was 0.61, 0.85, 0.65, 0.89, 0.88, 0.77 and 0.79, respectively ( $p < 0.001$ ). This indicated that diesel vehicles represented not only a significant contributor of OC and EC, but also a dominant source of  $PM_{2.5}$  mass. The correlation coefficients were 0.64 for EC1 and 0.63 for OC with the number of gasoline vehicles, indicating gasoline also significantly contributes to OC and EC. However, there was no positive correlation between these variables and the number of LPG vehicles, indicating that the LPG vehicle was not a significant contributor to OC and EC. These results are identical with the observation of source-dominated samples; i.e., diesel exhaust has a larger contribution to OC and EC than those from LPG and gasoline vehicles. OC showed good correlations with seven carbon fractions (OC1, OC2, OC3, OC4, EC1, EC2 and OP) except EC3. EC also had good correlations with seven fractions, except EC3. In other words, seven major fractions had good linear relationships. This implied that all six carbon fractions (OP was formed during the analysis) were emitted from the same source (diesel exhaust) and that none had undergone photochemical reactions, due to the close proximity of the monitoring station to the heavy traffic. There were good relationships between the OC2, EC1, EC2, OC, EC and mass with the ambient temperature. This is because there were more diesel vehicles in the daytime with high temperature and fewer diesel vehicles at night. In Table 2, wind speed did not seem to be an important factor for  $PM_{2.5}$  mass, OC, and EC because these concentrations were not reduced linearly by increasing wind speed from the correlation coefficients.



**Fig. 6.** Distribution of the concentration and percentage of eight carbon fractions in diesel-, gasoline-, and LPG-vehicle exhaust.



**Fig. 7.** Diurnal variations of eight fractions of OC/EC in the weekday and weekend.

## CONCLUSIONS

Measurements of fine particulate carbon and its eight fractions were made in close vicinity with a high traffic road around Hong Kong. High levels of  $PM_{2.5}$  mass, organic carbon and elemental carbon observed in a monitoring station (less than 1 m from the highway curb) to obtain a substantial quantity of data relating to freshly-emitted vehicular exhaust particles. The relationships between the concentrations of  $PM_{2.5}$ , OC, and EC traffic volume indicated that EC and OC were the main constituents of  $PM_{2.5}$ , and that the concentrations of EC and OC significantly increased with the increase in the number of diesel vehicles. Carbon profiles from source-dominated samples (diesel, LPG and gasoline vehicles) and the diurnal variations of eight carbon fractions indicated that EC2 and OC2 were mainly derived from diesel exhaust, and that OC3 and OC2 were largely from LPG and gasoline exhaust. As a consequence, carbon fractions from IMPROVE protocol could be used to identify different carbon sources.

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