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# Contributions of vehicular carbonaceous aerosols to PM<sub>2.5</sub> in a roadside environment in Hong Kong

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#### Abstract

Hourly measurements of elemental carbon (EC) and organic carbon (OC) were made at Mong Kok, a roadside air quality monitoring station in Hong Kong for a year from May 2011 to April 2012. The monthly average EC concentrations were 3.8–
4.9 μgCm<sup>-3</sup>, accounting for 9.2–17.7% of the PM<sub>2.5</sub> mass (21.5–49.7 μgm<sup>-3</sup>). The EC concentrations showed little seasonal variation and peaked twice daily in coincidence with the traffic rush hours of a day. Good correlations were found between EC and NO<sub>x</sub> concentrations, especially during the rush hours in the morning. In time periods when diesel-powered vehicles dominated the road traffic, the OC/EC ratio was approximately 0.5. The analysis by the minimum OC/EC ratio approach to determine OC/EC ratio representative of primary emissions also yields a value of 0.5, suggesting that it is a reasonable lower limit estimation of (OC/EC)<sub>vehicle</sub> in representing vehicular emissions. By applying the derived (OC/EC)<sub>vehicle</sub> ratio to the dataset, the monthly average vehicle-related OC was estimated to account for 16.6–64.0% of the mea-

- <sup>15</sup> sured OC throughout the year. Vehicle-related OC was also estimated using receptor modeling of a combined dataset of hourly  $NO_x$ , OC, EC and select volatile organic compounds. The estimations by the two different approaches were in good agreement. When both EC and vehicle-derived organic matter (OM) (assuming an OM-to-OC ratio of 1.4) are considered, vehicular carbonaceous aerosols contributed ~ 7.3 µgm<sup>-3</sup> to
- <sup>20</sup>  $PM_{2.5}$ , accounting for ~ 20 % of  $PM_{2.5}$  mass (38.3 µgm<sup>-3</sup>) during winter when Hong Kong was largely influenced by regional transport of air pollutants and ~ 30 % of  $PM_{2.5}$ mass (28.2 µgm<sup>-3</sup>) during summertime when local emission sources were dominant. A reduction of 3.82 µgm<sup>-3</sup> in vehicular carbonaceous aerosols was observed during 07:00–11:00 LT (i.e. rush hours on weekdays) on Sundays and public holidays. This
- <sup>25</sup> could mainly be attributed to less on-road public transportation (e.g. diesel-powered buses) in comparison with non-holidays. These multiple lines of evidence confirm local vehicular emissions as an important source of PM in an urban roadside environment





and suggest the importance of vehicular emission control in reducing exposure to  $PM_{2.5}$  in busy roadside environments.

#### 1 Introduction

- Carbonaceous species is an important constituent of the PM<sub>2.5</sub> (atmospheric particulate matter with aerodynamic diameters less than 2.5 μm) (Seinfeld and Pandis, 1998) and a substantial contributor to climate forcing, visibility impairment and adverse health effects (e.g. USEPA, 2004; IPCC, 2007). The carbonaceous material is commonly distinguished in elemental carbon (EC) and organic carbon (OC). EC has an exclusive origin in primary emissions from combustion of carbonaceous matter such as diesel,
- gasoline, biomass and organic wastes. In particular, EC dominates the particle fraction of diesel engine exhaust, which has recently been reclassified as carcinogenic to humans (e.g. USEPA, 2002; IARC, 2012). Since EC undergoes little chemical transformation in the atmosphere, it is a good indicator for primary combustion emissions. OC can be directly generated from primary emission sources (known as primary OC, DC can be directly generated from primary emission sources (known as primary OC, DC).
- POC) or formed through oxidation of reactive organic gases followed by gas-to-particle conversion processes in the atmosphere (known as secondary OC, SOC) (Gelencsér, 2004).

A significant fraction of PM<sub>2.5</sub> mass, ranging from approx. 16% in rural areas to around 40% in urban/roadside areas was identified in Hong Kong (DRI, 2010; HKUST, 2013). A clear regional-urban-street gradient of total carbon (TC) concentrations has been consistently observed within Hong Kong during the past decade and the higher EC concentrations at street level suggest the important contribution from traffic emissions. While there are some efforts of estimating the relative contributions of vehicular emissions to the PM mass and its organic fraction in Hong Kong, studies related to roadside PM sources are more limited. Zheng et al. (2006) analyzed filter samples collected at three contrasting sampling sites in respect to vehicular emission influence during 2000–2001. They employed a chemical mass balance receptor model in combi-



nation with organic tracers to identify nine air pollution sources. The contributions from vehicular emissions to the observed OC were reported to be approximately 70% at roadside site, 60% at urban site and 25% at rural site. Guo et al. (2009) applied principal component analysis with absolute principal component scores technique to the

- <sup>5</sup> PM<sub>2.5</sub> composition data obtained from two one-year studies in Hong Kong and showed that vehicle emissions contributed about 51 %, 23 % and 20 % to the PM<sub>2.5</sub> mass at roadside, urban site and rural site, respectively. Hu et al. (2010) analyzed high-volume PM<sub>2.5</sub> samples collected at four sites during the summer of 2006 and used positive matrix factorization and chemical mass balance models to apportion the source con-
- tributions to OC. The results showed that vehicular exhaust contributed 41.0% and 8.4% to the ambient OC on sampling days that were mainly under the influence of local emissions and regional transport, respectively. It is noted that these analyses were all based on 24 h filter measurements and they are inherently incapable of capturing the dynamics of pollutant emissions and atmospheric chemical conversion processes.
- <sup>15</sup> The Hong Kong Government has recognized the street-level air pollution as one of the most important air pollution issues for Hong Kong and has taken a wide range of measures to control the vehicular emissions (HKEPD, 2013). Continuous efforts are in urgent need to improve estimation of the various source contributions for the purpose of formulating effective control measures to lower the roadside PM.

In this study, one set of semi-continuous thermal/optical carbon field analyzer was deployed and operated at Mong Kok (MK), one of the three roadside air quality monitoring stations (AQMS) in Hong Kong. Measurements of hourly OC and EC concentrations were conducted for a year from May 2011 to April 2012. These high-time resolution OC and EC data were analyzed in detail for their diurnal, weekly, monthly and sea-

sonal variations. Attempts were made to derive the OC/EC ratio representing primary emissions at this roadside site and to estimate the concentration levels of vehicular carbonaceous aerosols together with its relative contributions to the PM<sub>2.5</sub> mass.





#### 2 Experimental

#### 2.1 Sampling equipment and method

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One set of semi-continuous OC-EC field analyzer system (RT-3131, Sunset Laboratory, OR, USA) was installed at MK AQMS, a roadside site located in a mixed residen-

tial and commercial area in Hong Kong with heavy traffic and surrounded by many tall buildings. The sampling inlet is about 2 m above ground and ambient air was drawn through a 2.5 μm aerodynamic diameter cut point cyclone at a flow rate of 8.2 Lmin<sup>-1</sup>. A carbon-impregnated parallel plate organic denuder is placed upstream of the analyzer for removing gaseous organics. The analyzer was programmed to collect particle
 samples for 46 min at the start of each hour, followed by a 9 min sample analysis and 3 min instrument stabilizing process.

The thermal/optical analytical method is based on the modified National Institute for Occupational Safety and Health (NIOSH) method 5040 protocol (Turpin et al., 1990; Birch and Cary, 1996; NIOSH, 2003). During the thermal analysis, the sample de-

- <sup>5</sup> posited on the quartz fiber filter punch is heated under different conditions and converted to CO<sub>2</sub> for detection by the non-dispersive infrared (NDIR) detector. In the first stage, thermal ramping occurs in a helium (He) environment from room temperature to 840 °C to volatize OC. The temperature of the front oven is then reduced to 550 °C. In the second stage, the carrier gas is switched to oxygen in helium (O<sub>2</sub>/He) and the
- temperature is increased stepwise to 870 °C, oxidizing off all of the EC in the sample. The temperature profiles and purge gases in each analysis stage is presented in Table S1. Since a fraction of the OC could be pyrolyzed under the O<sub>2</sub>-free conditions, a tuned diode laser (660 nm) is used to monitor the light transmission during the thermal analysis. In a typical analysis, the laser transmittance signals would firstly decrease due to
- the pyrolysis of OC. Then the pyrolyzed OC is oxidized in the presence of  $O_2$  and the transmittance would increase. When the laser signal reaches its initial value, this sets the split point differentiating OC and EC.

Ultra-high purity grade gases (He,  $10 \% O_2$  in He and  $5 \% CH_4$  in He) were used. To remove trace amounts of  $O_2$ , the He gas was purified through an  $O_2$  trap (SGT Middelburg V. V., the Netherlands) before use. The quartz fiber filters were pre-baked inside the main oven of the instrument at 870 °C for about 5 min before collection and were replaced on a weekly basis.

#### 2.2 Quality control and data validation

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The semi-continuous carbon analyzer collected samples approximately 90% of the time between 1 May 2011 and 30 April 2012. No data were collected during 21 June–20 July 2011 due to instrument maintenance and during 23–30 August 2011 due to NDIR malfunction.

The analyzer computer was closely monitored through a secured phone line and the instrument was checked daily for any error flags for hardware or software problems. Weekly routine instrument maintenance work includes sample filter replacement, cyclone cleaning, one-point external calibration, gas-flow checking and instrument blank.

- The study-average instrument blank ranged from 0.02 to 0.25 μgC for total carbon (TC) with an average of 0.13 μgC. For the 1 h measurement (46 min sampling at a flow rate of 8.2 Lmin<sup>-1</sup>), the blank values correspond to atmospheric concentrations of 0.05–0.66 μgCm<sup>-3</sup> (average of 0.60 μgCm<sup>-3</sup>). The method detection limits (MDLs) for OC and EC were then determined by three times the blank standard deviation as 0.60
- and 0.20 µgCm<sup>-3</sup>, respectively. Multi-point external calibrations were conducted once every 1–2 months. The external calibration was carried out through the analysis of known sucrose concentrations on a prebaked filter. Recommended by the manufacturer, 21.03 µgC was used for one point calibration while 4.21, 21.03 and 42.07 µgC were used for multi-point calibration. The recoveries of these three sucrose standard
- <sup>25</sup> solutions were 119.0±8.4, 100.7±6.0 and 95.3±7.1 %, respectively. When the organic denuder was changed once every two months, the sampling flow rate calibration was performed and the actual flow rates were recorded within  $8.2\pm0.4$  L min<sup>-1</sup>. Several experiments were conducted to determine the dynamic blank by placing a 47 mm Teflon





filter upstream of the denuder and sampling particle-free ambient air into the analyzer on a 2 h collection/analysis cycle. The average dynamic blank was  $0.46-0.83 \mu g C m^{-3}$ with an average of  $0.68 \mu g C m^{-3}$ , which corresponds to 8.7% of the measured OC (annual mean value). This value is consistent with the results from previous studies (e.g. Polidori et al., 2006; Kang et al., 2010) and supports the findings from Turpin et al. (1994) that the adsorption artifact is dependent on the concentrations of gaseous OC/particulate OC. On the other hand, the volatilization of particulate OC from the sampling quartz fiber filter was estimated to be  $10 \pm 6\%$  (upper limit) (Polidori et al., 2006).

Considering that the positive and negative artifacts are of comparable magnitude, no correction was made to the measured OC concentrations in this study. The results from dynamic blank test serve as an estimate of adsorption effect for the semi-continuous carbon analyzer running in MK AQMS.

The measurement data validation processes include checking of sampling volume, calibration peak area, NDIR signals and OCEC split point. Samples with a sampling volume variation beyond the tolerance of 5 % (i.e., 377 ± 20 L) or a calibration peak area variation beyond the tolerance of 10 % were considered to be invalid and excluded from the dataset. The raw data files of all the collected samples were inspected in order to confirm the OCEC split point (i.e. the time when the laser signal return to its initial value after the pyrolysis). The calculation software of the instrument was then used to process the raw data files with the split point being set manually. The data valid rate for the entire sampling period is approx. 96 %. The effective sampling duration, data capture rates and valid rates for individual month are listed in Table S2 in the Supplement.

The semi-continuous OC and EC measurements (also abbreviated as RT measure-<sup>25</sup> ments for ease of discussion) were further validated by comparing with OC and EC data obtained from two sets of off-line filter-based measurements. One is from the Hong Kong PM<sub>2.5</sub> speciation network program. In the speciation monitoring program, PM<sub>2.5</sub> samples were collected on prebaked 47 mm quartz fiber filters over a 24 h (starting from 00:00 LT at midnight) period by a Partisol sampler (Rupprecht & Patachnick, Model





2025, NY, USA). The 24 h filter-based measurements using the Partisol samplers, abbreviated as Partisol-TC, Partisol-OC and Partisol-EC hereafter, were made every 6th day throughout the year. The other one is from the PM<sub>2.5</sub> organic speciation project.  $PM_{25}$  samples were collected on prebaked 20 cm  $\times$  25 cm quartz fiber filters over a 24 h (starting from 00:00 LT at midnight) period by a High-Volume (HV) PM<sub>2.5</sub> particulate 5 sampler (Tisch Environmental Inc., OH, USA) at a frequency of once every three days. The HV sampler derived measurements were abbreviated as HV-TC, HV-OC and HV-EC hereafter. The sampled filters from both projects were stored in a freezer below -20°C after collection and were analyzed by a lab-based thermal/optical carbon analyzer (Sunset Laboratory, OR, USA) using the ACE-Asia protocol (Schauer et al., 10 2003), which is a variant of NIOSH protocol (Wu et al., 2012). The hourly OC and EC concentrations from the semi-continuous measurements were averaged over the same 24 h period to compare with the filter-based concentrations. The comparisons between the semi-continuous and the two sets of filter-based concentrations are shown in Fig. 1.

<sup>15</sup> The differences between the measurements were evaluated by zero-intercept linear regression, average percent relative bias (% RB) and average percent relative standard deviation (% RSD). The % RB and % RSD are calculated using the following equations,

$$\overline{C_{i}} = \frac{X_{i} + Y_{i}}{2}$$

$$\% RB_{i} = \frac{(Y_{i} - X_{i}) \times 100\%}{\overline{C_{i}}}$$

$$\% \overline{RB} = \frac{1}{n} \sum_{i=1}^{n} \frac{(Y_{i} - X_{i}) \times 100\%}{\overline{C_{i}}}$$

$$\% RSD_{i} = \frac{|\% RB_{i}|}{\sqrt{2}}$$

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(1)

(2)

(3)

(4)

$$\% \overline{\text{RSD}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \% \text{RSD}_{i}^{2}}$$

(5)

where the x and y are the comparative concentration values from different datasets and n is the total number of samples.

- The comparison results showed that the TC concentrations from semi-continuous 5 method agree fairly well with both Partisol filter measurements ( $R^2 = 0.98$ ,  $\% \overline{RB} =$ -29.6 %,  $\% \overline{\text{RSD}}$  = 23.4 %) and high-volume filter measurements ( $R^2$  = 0.99,  $\% \overline{\text{RB}}$  = -16.4%, %RSD = 15.2%). The Y/X ratios average at 0.75 ± 0.11 and 0.86 ± 0.11 for RT vs. Partisol samples and RT vs. HV samples, respectively, suggesting that in general the TC measurements from off-line filter samples were larger than those observed 10 by the semi-continuous method. In addition to the uncertainties associated with the sampling and analysis processes, the difference in sampling time also likely contribute to the discrepancy. The semi-continuous analyzer collected PM samples for a total of 1104 min on a daily basis, accounting for about 3/4 of the 24 h period. The high carbon concentrations with large variations at MK could be responsible for the approx. 15 15% difference between the semi-continuous measurements and the integrated filter analysis results. Fairly good correlations were also observed for all the OC measurements ( $R^2 = 0.97$ ,  $\%\overline{RB} = -33.8\%$ ,  $\%\overline{RSD} = 27.7\%$  for RT-OC vs. Partisol-OC and  $R^2 = 0.98$ ,  $\% \overline{\text{RB}} = -17.9\%$ ,  $\% \overline{\text{RSD}} = 18.4\%$  for RT-OC vs. HV-OC) but EC data com-
- parisons showed a certain degree of scatter. The average *Y/X* ratios for EC were 0.88±0.26 and 1.04±0.38 for RT vs. Partisol samples and RT vs. HV samples, respectively. The poor agreement between thermal EC from the semi-continuous analyzer and filter-based EC has been reported in several studies, especially at low concentration levels (e.g. Bae et al., 2004; Venkatachari et al., 2006). However, the discrepancies
   between RT-EC and filter-based EC for the roadside in this study might instead be due
- to the sampled air by the RT-ECOC analyzer not fully representing the 24 h integrated sampling period by the filter-based measurements. The sampled air masses were likely





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not well mixed since the sampling site is within a few meters of the on-road vehicular sources.

#### 3 Results and discussions

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#### 3.1 Organic and elemental carbon concentrations

- <sup>5</sup> The annual average OC and EC concentrations at MK AQMS during the study period were 7.82 and 4.36 μgCm<sup>-3</sup>, respectively. The average OC and EC concentrations in individual months and in different seasons during the study period are shown in Fig. 2. Based on the local meteorological characteristics, the seasons were defined as follows: 16 March–15 May as spring; 16 May–15 September as summer; 16 September– 15 Name and 10 Name and 15 May at 5 March 25 March 26 March
- <sup>10</sup> 15 November as fall and 16 November–15 March of the next year as winter (Chin, 1986; Yuan et al., 2006).

The monthly and seasonal variations of OC and EC showed that the OC concentrations varied among different seasons, with higher values in the winter months (November–February) and the lowest values were recorded in summertime (June– August). In comparison, EC concentrations exhibited little seasonal variations, suggesting that it dominantly came from local emission sources. The relative contributions of OC to  $PM_{2.5}$  ranged from 15.5 % (July 2011) to 29.3 % (January and February 2012) while EC contributed the most to PM mass in summer (17.7 % in June 2011) and least

in winter month (9.2% in December 2011). This can be explained by the quite comparable EC concentrations throughout the year together with the much lower  $PM_{2.5}$ concentrations during summertime.

The weekly patterns of carbon concentrations showed that the average EC concentrations were elevated on weekdays and decreased to a minimum on Sundays for all the months. The OC concentrations also had the lowest values on Sundays compared

to the rest of the week but the variations were less distinct than those of EC. These patterns were consistent with the traffic flow variation within the week and suggest that

emissions from motor vehicles were an important source for both OC and EC. In addition, unlike the EC concentrations which maintained at a quite stable level during the study period, the OC concentrations were evidently higher in winter months. It indicates the prominent influence of air pollutants which were transported into the MK area from s elsewhere.

The diurnal variations of carbon concentrations for weekdays (Monday–Friday), Saturdays, and holidays (Sunday and public holidays) were examined for individual months (Figs. S1 and S2) and four months were selected to represent the different seasons (Fig. 3, August for summer, October for fall, January for winter and March for spring).

- <sup>10</sup> The difference of OC concentrations between weekdays and holidays were more significant in summer than those in the other seasons. It is likely due to that in summer, OC observed in the sampling area was dominated by local sources such as vehicular exhaust, cooking, etc. These activities were reduced on holidays (e.g. reduced bus schedule) thus the concentrations of primary OC were lower. In winter and the two
- transitional seasons, on the other hand, the air pollutants were largely transported from elsewhere outside Hong Kong, leading to the less dependence of OC concentrations on the local sources. Different from the variation patterns of OC, EC concentrations were always found to be lower during holidays, indicating the "local" characteristics of its major sources.

The diurnal profiles are also quite different for OC and EC. EC concentrations started to increase from 07:00 LT in the morning and two peaks (07:00–11:00 LT and 16:00– 19:00 LT) were observed during the day. These two periods with higher EC concentrations is a result of vehicular emissions since they coincided with the rush hours. Starting from 19:00 LT, EC concentrations decreased and then remained at a relatively

<sup>25</sup> low level from midnight till the next early morning. It is also found that the NO<sub>x</sub> and EC concentrations correlate quite well with each other especially during the time period of 09.00 p.m.–06.00 a.m. (the next day) and the first rush hour period (Fig. 4). In these two periods, the emission sources at roadside were relatively limited and the observed EC and NO<sub>x</sub> would be primarily from vehicular exhaust. During the rest of the day by con-





trast, the various emission sources for  $NO_x$  together with the higher reactivity of  $NO_x$  during daytime could lead to a weaker correlation between  $NO_x$  and EC concentrations.

The OC concentrations also peaked twice a day (11:00–16:00 LT and 19:00–22:00 LT). The diurnal profile comparison between OC and  $O_3$  showed that one  $O_3$ 

- peak commonly appeared in the early afternoon but was ~1–2 h earlier than the afternoon OC peak (Fig. 5). Since ozone could be an indicator of photochemical processes in the atmosphere, it is suggested that the first OC peak observed in the afternoon was related to the secondary organic aerosol (SOA) formation. The nighttime OC peak, on the other hand, could be associated with emissions from the larger number of private
   cars on the road. In addition, the cooking-related activities are believed to contribute to
  - the higher OC levels during both of the time periods.

The different diurnal variations of OC and EC concentrations result in an OC/EC ratio pattern of three peaks appearing during the day. The first one is observed in the early morning when EC concentrations were much lower than those of OC. The second

peak appeared in the early afternoon, coinciding with the first OC peak. The third peak was at around 20:00 LT in the evening when the OC concentrations were high while EC concentrations started to decrease.

#### 3.2 Estimation of the (OC/EC)<sub>vehicle</sub>

The EC-tracer method is the simplest approach to estimate the contributions of primary
 and secondary sources to measured particulate OC (e.g. Chu and Macias, 1981; Wolff et al., 1982; Turpin et al., 1991; Turpin and Huntzicker, 1995; Cabada et al., 2004; Chu, 2005; Plaza et al., 2006; Lonati et al., 2007). This method is based on the assumption that EC is exclusively primary in origin and that EC and primary OC have common emission sources (e.g. combustion, resuspension of combustion particles, etc.). The
 total OC concentration is the sum of POC and SOC:

[OC]<sub>measured</sub> = [OC]<sub>primary</sub> + [OC]<sub>secondary</sub>





(6)

POC is emitted mainly by combustion or combustion-related sources, but there is also a minor non-combustion portion which comes from non-combustion sources (e.g. biogenic sources), therefore,

 $_{5}$  [OC]<sub>primary</sub> = [OC]<sub>combustion</sub> + b

where b denotes non-combustion primary OC.

By using  $(OC/EC)_{pri}$  as the concentration ratio of OC and EC from combustion sources and measured [EC] and [OC], the POC and SOC can be calculated as follows,

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$$[OC]_{primary} = EC \times (OC/EC)_{pri} + b$$
 (8)

$$[OC]_{secondary} = [OC]_{measured} - [EC \times (OC/EC)_{pri} + b]$$

It can be seen that (OC/EC)<sub>pri</sub>, the OC to EC ratio characteristic of primary emissions, plays a key role in estimating the SOC contribution when using the EC-tracer <sup>15</sup> method. Several approaches have been proposed to estimate the (OC/EC)<sub>pri</sub>. These approaches include estimating the primary OC/EC ratio using (1) emission inventories of OC and EC from primary sources (Gray et al., 1986); (2) ambient OC and EC measurements made when primary source emissions are dominant or/and when photochemical activities are weak (Turpin and Huntzicker, 1991) and (3) the minimum <sup>20</sup> OC/EC ratio obtained in the study period (Lim and Turpin, 2002).

The first attempt is to determine the primary OC/EC ratio using a subset of data that have a given percentage of the lowest OC/EC ratios among the complete data set (Castro et al., 1999). The slope  $((OC/EC)_{min})$  and the intercept (b) in Eq. (9) were calculated by Deming regressing OC on EC using the 5% data with lowest OC-to-EC

ratios. In the Deming regression analysis, the uncertainties in both x- and y-axis are assumed to be equal (Deming, 1943; Cornbleet and Gochman, 1979). The regressions were performed on a monthly, seasonal and annual basis so as to evaluate the robustness of different subsets of data (Table 1).



(7)

(9)



The obtained  $(OC/EC)_{min}$  ratios exhibited lower values during summer months. In particular, for July (0.41) and August (0.55), the intercepts were rather low while the correlations were the highest among all ( $R^2 > 0.97$ ). Higher values of  $(OC/EC)_{min}$  were observed for December 2011 (1.43,  $R^2 = 0.90$ ) and January 2012 (1.49,  $R^2 = 0.75$ ). The monthly variations of  $(OC/EC)_{min}$  are consistent with the estimations for different seasons. The lowest value (0.53,  $R^2 = 0.92$ ) was found in summer, which is a sea-

- son mainly under the influence of local primary emissions and from time to time the southerly winds from the ocean would bring in cleaner air to further dilute the pollution in Hong Kong. During winter season, the prevailing winds were northerly and north-
- easterly and the regional transport of air pollutants played a significant role. The higher (OC/EC)<sub>min</sub> ratio is possibly owing to primary sources having higher (OC/EC) and contribution of SOA in the 5% lowest (OC/EC) samples. Spring and fall are transitional seasons with prevailing winds as a combination of southerly and northerly and therefore the (OC/EC)<sub>min</sub> values were recorded to be in-between.
- <sup>15</sup> Since local primary emission sources are believed to be dominant during summertime, Deming regressions were performed on the OC and EC dataset obtained in summer, with the lowest (OC/EC) samples examined varying from 5 % to 100 % (Table 2). The slope gradually increases from 0.53 to 1.41 as data with increasingly higher OC/EC ratios are included. The intercept is always below or close to zero, suggest-
- ing that the non-combustion contribution was not significant during this period. Under this "local emissions-influenced" scenario, a value of 0.5 was suggested to represent a lower limit while 1.4 could serve as an upper limit to represent the primary OC/EC ratio in MK area.

To evaluate the impact of different emission sources on the OC/EC ratio, further attempt was made to examine the OC/EC ratios derived from data subsets selected using different criteria. According to the carbon diurnal profiles, three time periods were chosen for Deming regression analysis to estimate the corresponding OC/EC ratios (Table 3). These three periods include two EC peak times (07:00–11:00 LT in the morning and 16:00–19:00 LT in the afternoon) and one OC peak time (19:00–22:00 LT





in the evening). We note that data from the identified episodic periods (when the hourly PM<sub>2.5</sub> mass concentrations exceeded the monthly average plus one standard deviation for 4 h or more) were excluded since on episode days the carbon concentrations were considerably influenced by more aged air masses transported from outside-Hong 5 Kong.

The slopes obtained varied with months. Higher values were observed in fall and winter months, but usually with weaker correlations (lower  $R^2$ ), suggesting the presence of mixed OC and EC sources. In comparison, lower OC/EC ratios and stronger correlations were recorded for summer months (May–August). This is consistent with the hypothesis that local sources dominated in summertime while transported air masses largely impacted Hong Kong during winter leading to higher OC/EC ratios.

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Within the same month, the OC/EC ratios obtained from the two EC peak periods were comparable and were the highest from the periods of 19:00–22:00 LT. This is expected since the first two periods were dominated by vehicular emissions. In particular,

- <sup>15</sup> a trend of (OC/EC)<sub>7:00-11:00</sub> < (OC/EC)<sub>16:00-19:00</sub> < (OC/EC)<sub>19:00-22:00</sub> can always be observed for the summer months. One possible explanation is that during the first rushhour period of the day, public transportation (e.g. buses, light buses, good vehicles, etc.) were predominant on the road and most of them were diesel-powered vehicles. During the second rush-hour period, however, more private cars, which were predominately
- <sup>20</sup> powered by gasoline engines, were on the road. The OC/EC ratios were 0.6–0.8, as reported in the source profile for diesel engine exhaust (Hildemann et al., 1991; Schauer et al., 1999a), 2.2–4.2 for catalyst-equipped gasoline exhaust and 8.2–60.0 for noncatalyst gasoline-powered exhaust (Hildemann et al., 1991; Schauer et al., 2002a). The compositional variation in the on-road motor vehicles is expected to result in fairly dif-
- ferent OC/EC ratios. On the other hand, the consistently higher (OC/EC)<sub>19:00-22:00</sub> is suspected to be caused by both motor vehicles and cooking-related activities. Previous studies on cooking source samples revealed that little EC were emitted from cooking while OC accounted for 34–69 % of the emitted PM<sub>2.5</sub> mass (Hildemann et al., 1991;





Schauer et al., 1999b, 2002b). This primary OC source from cooking would certainly increase the measured OC/EC ratios.

The comparisons between the calculated  $(OC/EC)_{min}$  and  $(OC/EC)_{subsets}$  clearly shows that it is very difficult to derive a single value to represent the primary OC/EC

ratio since there are a variety of emission sources in the study area, each making time-varying contributions. Using the (OC/EC)<sub>min</sub> as the primary OC/EC ratio in the EC-tracer method would lead to overestimation of SOC during time periods when cooking-related sources dominate. However, a value of 0.5 can be proposed to reasonably represent the primary OC/EC ratio for vehicular emissions. Vehicle-related OC (i.e., OC<sub>vehicle</sub>) is therefore 0.5 × EC.

#### 3.3 Estimation of vehicle-related OC and PM

#### 3.3.1 Estimation using (OC/EC)<sub>vehicle</sub> inferred from OCEC measurements

The annual average vehicle-related OC (OC<sub>vehicle</sub>) concentration was 2.18 ± 1.20  $\mu$ gCm<sup>-3</sup>, which represents 32.0 ± 18.9% of the annual average particulate OC. The monthly average OC<sub>vehicle</sub> concentrations showed little variation throughout the 15 year  $(1.89-2.43 \,\mu \text{gCm}^{-3})$  while the percent contribution to total OC varied from 16.6% in December to 64.0 % in July. By applying a ratio of 1.4 to convert OC to organic matter (OM) (Malm et al., 1994), the daily-averaged contributions of vehicle-related organic aerosols ( $OM_{vehicle}$ ) to the PM<sub>2.5</sub> mass were estimated to be in the range of 3.5–24.8 %. By further summing up the concentrations of OM<sub>vehicle</sub> and EC, the vehicle-related car-20 bonaceous PM (PM<sub>vehicle</sub>) with its contributions to the PM<sub>2.5</sub> mass can be estimated. The monthly average  $PM_{vehicle}$  ranged from 6.46 to 8.27 µgCm<sup>-3</sup> and exhibited little seasonal variations (Fig. 6), indicating the local nature of vehicular emission source. Its relative contributions to the total PM<sub>2.5</sub> mass, on the other hand, varied from 16.0 % (December 2011) to 35.6% (August 2011) with an annual average of 24.8%. The per-25 cent contribution differences were mainly due to higher PM<sub>2.5</sub> levels during winter time as a result of additional air pollutants transported into Hong Kong from other regions.



Calculations also show that the average PM<sub>vehicle</sub> concentrations were estimated to be 10.29 µgm<sup>-3</sup> during the first rush hour period (07:00–11:00 LT) on non-holidays and 6.47 µgm<sup>-3</sup> for the same period on holidays (including Sundays and public holidays). A reduction of approx. 37 % in PM mass on holidays could be attributed to the reduced on-road public transportation (e.g. diesel-powered bus frequencies on Sundays and public holidays decrease by 20–30 % compared to the rest of the week). These results indicate that the emissions from on-road vehicles are an important source of PM in the urban roadside environment of Hong Kong.

#### 3.3.2 Estimation using receptor modeling analysis

- <sup>10</sup> The OC<sub>vehicle</sub> were also estimated by a receptor modeling approach so that comparisons can be conducted between the two data sets for further evaluation. In the receptor modeling approach, source apportioning was performed on OC and EC by Positive Matrix Factorization (PMF) Model. The input data consist of hourly concentrations of 27 volatile organic compounds (VOCs), NO, NO<sub>2</sub>, OC and EC. The VOC measure-
- <sup>15</sup> ments were conducted on an hourly/half-hourly basis using a GC955 series 611/811 VOC analyzer (Syntech Spectras, Netherlands) at MK AQMS. The isoprene data were excluded from the input dataset since the biogenic emissions at roadside can be neglected. Iso-hexane data were also excluded since more than 30% of the measurements were below the method detection limit.
- <sup>20</sup> The uncertainties for individual species were initially estimated as  $(s_{ij} + MDL_{ij}/3)$ (e.g., Polissar et al., 1998; Reff et al., 2007), where  $MDL_{ij}$  is the method detection limit and  $s_{ij}$  is the analytical uncertainty of the corresponding species in the data set. The analytical uncertainties were assumed to be 10 % of the species concentrations for most of the VOCs and 5 % for NO and NO<sub>2</sub>. The smaller molecules (i.e. ethane, ethane and ethyne) coelute in the GC analysis, causing larger uncertainties. A few VOCs (e.g.
- and ethyne) coelute in the GC analysis, causing larger uncertainties. A few VOCs (e.g. 1,3,5- and 1,2,3-trimethylbenzenes, butenes and pentenes) were detected in less than 90% of the samples. The uncertainties of these VOCs were increased by a factor of 3 in the PMF analysis. For data which are below the detection limits, the concentrations



were replaced with the value (MDL<sub>*ij*</sub>/2) and the corresponding uncertainty was set to  $((5/6) \times MDL_{ij})$  (Polissar et al., 1998).

The source apportioning modeling was performed using EPA PMF 3.0 software (available at http://www.epa.gov/heasd/research/pmf.html). This software provides the

- <sup>5</sup> bootstrap model which is based on the Monte Carlo principle to check the mathematical stability of selected runs (Norris et al., 2008). Each modeling run included 20 base runs and the base run with the minimum Q value was retained as the solution. Solutions for 4–9 factors were tested and the six-factor solution was considered to be the reasonable one. The source profiles of the six-factor solution are shown in Fig. 7.
- The first factor is rich in ethane, ethyne and benzene, all of which are relatively stable species. It is therefore suggested that this factor is associated with aged air mass which was transported from other places. During the aging processes, reactive compounds such as alkenes would decay more rapidly than unreactive species and the oxidative state of the aerosols would be increased (OC/EC ratio was observed to be higher than 2).

The second, third and sixth factors are all identified as vehicular emissions from diesel-powered and gasoline-powered engines. Factor 2 is proposed to be dominated by diesel exhaust as it is characterized by the presence of 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene. The three VOC species appeared in the distinct source profile of Hong Kong diesel fuel, as reported by Tsai et al. (2006). In particular, this factor is associated with the lowest OC/EC ratio (0.44) among all the factors, together with a large amount of NO. It is therefore postulated to be more related to freshly emitted diesel exhaust. Factor 3 is dominated by *i*-pentane, *n*-pentane, pentenes and three trimethylbenzenes. Since pentanes have been reported as markers

<sup>25</sup> of gasoline vapors in Hong Kong (Tsai et al., 2006) and the OC/EC ratio in this factor (1.13) is higher than that in factor 2, it is suggested that the third factor represents the better mixed air mass. Factor 6 is related to gasoline-powered engine exhaust, characterized by the presence of *i*-pentane which is the major component in gasoline vapor, and cis-2-butene and 1,3-butadiene which are two common indicators for vehi-





cle exhaust. The OC/EC ratio in this factor (2.36) is higher than those in the other two factors.

The fourth factor is distinguished by a large amount of toluene, benzene, ethylbenzene, xylenes,  $C_6$  and  $C_7$  alkanes. This source is considered to be a composite of emissions from solvent use, architectural paints and industrial activities (Seila et al., 2001; Chan et al., 2006). The industrial and architectural sources are an important source of aromatic VOCs, but they make limited contributions to particulate OC and EC at MK.

The fifth factor is dominated by propane, *i*-butane and *n*-butane, hence is identified as the emissions from the use of liquefied petroleum gas (LPG) in vehicles, gas stations and cooking activities (Blake and Rowland, 1995). It is noted that LPG combustion and vapors barely contributed to the carbon fraction in PM<sub>2.5</sub> since the light alkanes emitted from LPG are too volatile to reside in the particle phase.

On the basis of the source identifications, OC apportioned into factors 2, 3, 5 and 6 were summed up so as to represent the PMF-derived  $OC_{vehicle}$ . The comparison of daily  $OC_{vehicle}$  obtained from the EC-tracer method and the PMF approach is shown in a time series plot (Fig. 8). A fairly good agreement was observed between the estimations from the two methods ( $R^2 = 0.75$ ). On average, PMF-derived  $OC_{vehicle}$  were approximately 20% higher than those calculated by the EC-tracer method. The discrepancies could be due to one or a combination of the following reasons: (1) uncertainties of the PMF analysis; (2) uncertainty in the  $(OC/EC)_{vehicle}$  caused by the variation of the vehicle composition and (3) omission of the cooking-related OC.

The relative contributions of different vehicular emission sources to the  $OC_{vehicle}$  and EC were estimated by the PMF approach (Fig. 8, pie charts). The diesel-dominant

factor (Factor 2) contributed the most to EC and approximately one third to OC<sub>vehicle</sub>. The gasoline-dominant factor (Factor 6) contributed the least to EC but the most to OC<sub>vehicle</sub>. These estimations suggest that both diesel-powered and gasoline-powered vehicles are major contributing sources to the carbonaceous particle levels at roadside.





#### 4 Conclusions

PM<sub>2.5</sub> carbon measurements of hourly time resolution were conducted in the roadside environment of Hong Kong for the first time, over a 12 month period from May 2011 to April 2012. Three levels of validation were performed and the data valid rate for the
 <sup>5</sup> entire sampling period is approximately 96%. The OC and EC concentrations at MK AQMS during the study period were on average 7.82 and 4.36 µgCm<sup>-3</sup>, respectively. Higher OC concentrations were recorded during winter months as a result of the contributions of regional air pollutant transport. EC concentrations were comparable among individual months. In addition, the EC concentrations peaked in two time periods which
 <sup>10</sup> coincided with the traffic rush hours of a day. Both results indicate that EC was dominantly emitted from local vehicular sources.

The OC/EC ratio representing primary combustion emissions was estimated using the minimum OC/EC ratio approach and from selected data subsets. The results from both approaches showed that using a single value as the OC-to-EC ratio for primary

- emissions in order to estimate POC and SOC by EC-tracer method may cause significant biases since there were a variety of primary emission sources in the sampling area, each making time-varying contributions. On the other hand, a value of 0.5 can be proposed to reasonably approximate the primary OC/EC ratio for vehicular emissions. The annual average vehicle-related OC concentration was subsequently estimated to
- <sup>20</sup> be 2.18±1.20 µgCm<sup>-3</sup>, which accounted for 32.0±18.9% of the annual average particulate OC. The monthly average OC<sub>vehicle</sub> concentrations had a small variation throughout the year (1.89–2.43 µgCm<sup>-3</sup>) while its contribution to total OC varied from 16.6% (December 2011) to 64.0% (July 2011). The OC<sub>vehicle</sub> derived from source apportionment analysis by PMF are in good agreement with the estimates that are obtained by
- the proposed (OC/EC)<sub>vehicle</sub>, giving some confidence about the results. Assuming an OM-to-OC ratio of 1.4, the daily-averaged contributions of OM<sub>vehicle</sub> to PM<sub>2.5</sub> ranged from 3.5 to 24.8%. The annual average concentration of PM<sub>vehicle</sub> was estimated to





be 7.42  $\mu g \, m^{-3}$  and accounted for approx. 25 % of the PM\_{2.5} concentration, confirming vehicular emissions as an important source of PM mass.

The carbon diurnal profiles also suggest cooking-related activities as a potentially important source to OC in the study area. Special attention needs to be paid when EC-

tracer method with a constant primary OC/EC ratio is applied to estimate the relative contributions of POC and SOC since biases can be easily caused due to the neglect of other primary OC sources. Higher resolution measurements of particle-phase tracer compounds for the sources (e.g. C<sub>16</sub> and C<sub>18</sub> fatty acids as the tracers for cooking-related activities; phthalic acid as the tracer for vehicle-related SOA) could provide
 possibilities in a more accurate estimation of SOA contributions in the urban areas of Hong Kong.

## Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/57/2014/ acpd-14-57-2014-supplement.pdf.

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- <sup>20</sup> The content of this paper does not necessarily reflect the views and policies of the HKSAR Government, nor does mention of trade names or commercial products constitute an endorsement or recommendation of their use.





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**Table 1.** Deming regression results of  $(OC/EC)_{min}$  (the slope) and non-combustion term b (the intercept) on a monthly, seasonal and annual basis from the one-year carbon measurements at MK AQMS.

Time period	No. of data	(OC/EC) <sub>min</sub> (slope)	Non-combustion term b (intercept)	Correlation coefficient $(R^2)$
May 2011	34	0.72	0.23	0.83
Jun 2011	24	0.76	-2.16	0.61
Jul 2011	12	0.41	-0.31	0.98
Aug 2011	24	0.55	-0.37	0.97
Sep 2011	36	0.41	1.45	0.77
Oct 2011	38	0.71	0.18	0.83
Nov 2011	36	0.58	1.03	0.43
Dec 2011	36	1.43	0.03	0.90
Jan 2012	38	1.49	-1.05	0.75
Feb 2012	36	0.98	0.26	0.93
Mar 2012	34	0.71	1.14	0.82
Apr 2012	36	0.21	2.58	0.32
Summer	94	0.53	-0.42	0.92
Fall	72	0.64	0.29	0.81
Winter	142	1.06	-0.64	0.71
Spring	66	0.61	0.25	0.66
Year	372	0.71	-0.80	0.83



**Discussion Paper** 

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(cc)

Table 2. Deming regression results for hourly OC and EC concentrations grouped by OC/ECratio for summer sampling at MK AQMS.

Lowest % by OC/EC	No. of data	(OC/EC) <sub>min</sub> (slope)	Non-combustion term b (intercept)	Correlation coefficient ( $R^2$ )
5	94	0.53	-0.42	0.92
10	188	0.63	-0.62	0.88
20	376	0.75	-0.78	0.78
30	564	0.90	–1.13	0.74
40	752	0.90	-0.80	0.71
50	940	0.97	-0.82	0.67
60	1128	1.14	-1.29	0.66
70	1316	1.24	-1.44	0.62
80	1504	1.38	-1.73	0.59
90	1692	1.41	-1.45	0.53
100	1878	1.15	0.05	0.48

**Table 3.** Estimated  $(OC/EC)_{pri}$  ( $R^2$  in parentheses) by Deming regression of OC on EC from time periods of 07:00–11:00 LT, 16:00–19:00 LT and 19:00–22:00 LT for individual months at MK AQMS.

Month	Time period				
	07:00-11:00 LT	16:00–19:00 LT	19:00–22:00 LT		
May 2011	0.96 (0.91)	1.15 (0.90)	2.28 (0.78)		
Jun 2011	0.61 (0.95)	0.84 (0.91)	1.67 (0.91)		
Jul 2011	0.57 (0.93)	0.73 (0.94)	1.42 (0.96)		
Aug 2011	0.75 (0.92)	0.80 (0.92)	1.52 (0.87)		
Sep 2011	1.46 (0.47)	0.44 (0.36)	1.52 (0.63)		
Oct 2011	1.33 (0.54)	1.37 (0.30)	2.20 (0.43)		
Nov 2011	1.94 (0.56)	1.40 (0.74)	4.11 (0.53)		
Dec 2011	2.55 (0.74)	2.13 (0.63)	3.27 (0.75)		
Jan 2012	1.72 (0.65)	1.49 (0.78)	2.46 (0.84)		
Feb 2012	1.15 (0.81)	0.89 (0.63)	2.05 (0.62)		
Mar 2012	0.96 (0.87)	1.13 (0.59)	2.26 (0.75)		
Apr 2012	1.38 (0.48)	1.74 (0.56)	8.56 (0.26)		





**Fig. 1.** Scatter plots of semi-continuous measurements vs. filter-based chemical data for  $PM_{2.5}$  samples collected at MK AQMS during May 2011–April 2012. (a) RT-TC vs. Partisol-TC by TOT; (b) RT-OC vs. Partisol-OC by TOT; (c) RT-EC vs. Partisol-EC by TOT; (d) RT-TC vs. HV-TC by TOT; (e) RT-OC vs. HV-OC by TOT and (f) RT-EC vs. HV-EC by TOT.







**Fig. 2.** The 1 h OC and EC concentrations in individual sampling months and in different seasons at MK AQMS during the study period from May 2011 to April 2012 (the box length: the 25th and the 75th percentiles; the whiskers: the 10th and the 90th percentiles; the dot in the box: the average; the line in the box: the median; the circles: the minimum and maximum values).













Fig. 4. Diurnal variations of EC ( $\mu g C \, m^{-3})$  and NO\_x ( $\mu g \, m^{-3})$  at MK AQMS during different seasons.







Fig. 5. Diurnal variations of OC ( $\mu$ gCm<sup>-3</sup>) and O<sub>3</sub> ( $\mu$ gm<sup>-3</sup>) at MK AQMS during different seasons.







**Fig. 6.** Monthly average vehicle-related PM concentrations estimated by  $(OM_{vehicle}+EC)$  and the relative contributions to the monthly average  $PM_{2.5}$  mass at MK AQMS during May 2011– April 2012. (Note:  $PM_{2.5}$  mass concentrations were measured by a Tapered Element Oscillating Microbalance (TEOM 1400AB) on an hourly basis.)





Fig. 7. Source profile (% of species total) identified by USEPA PMF3.0.







**Fig. 8.** Time-series daily-averaged  $OC_{vehicle}$  ( $\mu$ gCm<sup>-3</sup>) estimated by EC-tracer method (blue curve) and by PMF approach (red curve) at MK AQMS during May 2011–April 2012. The relative contributions of different vehicular emission-related factors to the  $OC_{vehicle}$  and EC, estimated by PMF, are shown in the pie charts.



