

Contributions of vehicular carbonaceous aerosols to PM_{2.5} 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 $\mu\text{gC}/\text{m}^3$, accounting for 9.2–17.7% of the PM_{2.5} mass (21.5–49.7 $\mu\text{g}/\text{m}^3$). The EC concentrations showed little seasonal variation and peaked twice daily coinciding with the traffic rush hours of a day. Strong correlations were found between EC and NO_x concentrations, especially during the rush hours in the morning, confirming vehicular emissions as the dominant source for EC at this site. The analysis by the minimum OC/EC ratio approach to determine OC/EC ratio representative of primary vehicular emissions yields a value of 0.5 for (OC/EC)_{vehicle}. By applying the derived (OC/EC)_{vehicle} ratio to the dataset, the monthly average vehicle-related OC was estimated to account for 17–64% of the measured OC throughout the year. Vehicle-related OC was also estimated using receptor modeling of a combined dataset of hourly NO_x, OC, EC and volatile organic compounds characteristic of different types of vehicular emissions. The OC_{vehicle} 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 $\sim 7.3 \mu\text{g}/\text{m}^3$ to PM_{2.5},

31 accounting for ~20% of PM_{2.5} mass (38.3 µg/m³) during winter when Hong Kong received
32 significant influence of air pollutants transported from outside and ~30% of PM_{2.5} mass (28.2
33 µg/m³) during summertime when local emission sources were dominant. A reduction of 3.8
34 µg/m³ in vehicular carbonaceous aerosols was estimated during 7:00–11:00 (i.e. rush hours
35 on weekdays) on Sundays and public holidays. This could mainly be attributed to less on-
36 road public transportation (e.g. diesel-powered buses) in comparison with non-holidays.
37 These multiple lines of evidence confirm local vehicular emissions as an important source of
38 PM_{2.5} in an urban roadside environment and suggest the importance of vehicular emission
39 control in reducing exposure to PM_{2.5} in busy roadside environments.
40

41 **1 Introduction**

42 Carbonaceous species is an important constituent of the PM_{2.5} (atmospheric particulate matter
43 with aerodynamic diameters less than 2.5 µm) (Seinfeld and Pandis, 1998) and a substantial
44 contributor to climate forcing, visibility impairment and adverse health effects (e.g. USEPA,
45 2004; IPCC, 2007). The carbonaceous material is commonly distinguished in elemental
46 carbon (EC) and organic carbon (OC). EC has an exclusive origin in primary emissions from
47 combustion of carbonaceous matter such as diesel, gasoline, biomass and organic wastes. In
48 particular, EC dominates the particle fraction of diesel engine exhaust, which has recently
49 been reclassified as carcinogenic to humans (e.g. USEPA, 2002; IARC, 2012). EC has been
50 considered to undergo little chemical transformation in the atmosphere, and thus it has been
51 used as an indicator for primary combustion emissions. OC can be directly generated from
52 primary emission sources (known as primary OC, POC) or formed through oxidation of
53 reactive organic gases followed by gas-to-particle conversion processes in the atmosphere
54 (known as secondary OC, SOC) (Gelencsér, 2004).

55 A significant fraction of PM_{2.5} mass, ranging from 16% in rural areas to around 40% in
56 urban/roadside areas, was identified in Hong Kong (DRI, 2010; HKUST, 2013). A clear
57 regional-urban-street gradient from low to high in total carbon (TC) concentrations has been
58 consistently observed within Hong Kong during the past decade. The higher EC
59 concentrations at street level reflect the important contribution from traffic emissions. While
60 there exist a few studies examining the relative contributions of vehicular emissions to the
61 PM_{2.5} mass and its organic fraction in Hong Kong, fewer efforts have been focused on
62 roadside PM_{2.5} sources. Zheng et al. (2006) analyzed filter samples collected at three
63 contrasting sampling sites with respect to vehicular emission influence during 2000–2001.

64 They employed a chemical mass balance receptor model in combination with organic tracers
65 to apportion contribution of nine air pollution sources to PM_{2.5} OC. The contributions to OC
66 from vehicular emissions were reported to be approximately 70% at roadside site, 60% at
67 urban site and 25% at rural site. Guo et al. (2009) applied principal component analysis with
68 absolute principal component scores technique to the PM_{2.5} composition data obtained from
69 two one-year studies in Hong Kong and showed that vehicle emissions contributed about
70 51%, 23% and 20% to the PM_{2.5} mass at roadside, urban site and rural site, respectively. Hu
71 et al. (2010) analyzed high-volume PM_{2.5} samples collected at four sites during the summer
72 of 2006 and used positive matrix factorization and chemical mass balance models to
73 apportion the source contributions to OC. The results showed that vehicular exhaust
74 contributed 41.0% and 8.4% to the ambient OC on sampling days that were mainly under the
75 influence of local emissions and regional transport, respectively. These source analysis
76 studies were all based on 24-hr filter measurements and they are inherently incapable of
77 capturing the dynamics of pollutant emissions and atmospheric chemical conversion
78 processes that happen on a faster time scale.

79 The Hong Kong Government has recognized the street-level air pollution as one of the most
80 important air pollution issues for Hong Kong and has taken a wide range of measures to
81 control the vehicular emissions (HKEPD, 2013). Hence, continuous efforts are in urgent need
82 to monitor PM_{2.5} components closely related to vehicular emissions and to estimate their
83 contributions to PM_{2.5} mass for the purpose of evaluating and formulating control measures
84 targeting lowering the roadside PM_{2.5}.

85 In this study, a semi-continuous thermal/optical carbon field analyzer was deployed at Mong
86 Kok (MK), one of the three roadside air quality monitoring stations (AQMS) in Hong Kong.
87 Mong Kok, with its extremely high population density of 130,000 persons per km², is
88 described as the busiest district in the world by the Guinness World Records. Measurements
89 of hourly OC and EC concentrations were conducted for a year from May 2011 to April 2012.
90 These high-time resolution OC and EC data were analyzed to examine their diurnal, weekly,
91 monthly and seasonal variations. The objectives are to derive the OC/EC ratio representing
92 primary vehicular emissions and to estimate the contributions of vehicular carbonaceous
93 aerosols to PM_{2.5} in the roadside environment in Hong Kong.

94

95

96 2 Experimental

97 2.1 Sampling equipment and method

98 A semi-continuous OC-EC field analyzer system (RT-3131, Sunset Laboratory, OR, USA)
99 was installed at MK AQMS, a roadside site located in a mixed residential and commercial
100 district in Hong Kong with heavy traffic and surrounded by many tall buildings. At the MK
101 AQMS, a few aerosol samplers are located on a platform around 3 m above the ground level
102 and instruments for the criteria gas pollutants are housed in a room at the site with their inlets
103 extending through the ceiling. The ECOC analyzer used in this work was located on the
104 ground with the inlet ~2 m above the ground and ambient air was drawn through a 2.5 μm
105 aerodynamic diameter cut point cyclone at a flow rate of 8 L/min. A carbon-impregnated
106 parallel plate organic denuder is placed upstream of the analyzer for removing gaseous
107 organics. The analyzer was programmed to collect particle samples for 46 min at the start of
108 each hour, followed by a 9-min sample analysis and 3-min instrument stabilizing process.

109 The thermal/optical analytical method is based on the modified National Institute for
110 Occupational Safety and Health (NIOSH) method 5040 protocol (Turpin et al., 1990; Birch
111 and Cary, 1996; NIOSH, 2003). During the thermal analysis, the sample deposited on the
112 quartz fiber filter is heated under different conditions and carbonaceous materials in the
113 sample are converted to CO_2 for detection by the non-dispersive infrared (NDIR) detector. In
114 the first stage, thermal ramping occurs in a helium (He) environment from room temperature
115 to 840°C to volatilize OC, followed by a brief cooling step to 550°C. In the second stage, the
116 carrier gas is switched to oxygen in helium (O_2/He) and the temperature is increased stepwise
117 to 870°C, oxidizing off all of the EC in the sample. The temperature profiles and purge gases
118 in each analysis stage is presented in Table S1 in the supplementary material. Since a fraction
119 of the OC could be pyrolyzed under the O_2 -free conditions, a tuned diode laser (660 nm) is
120 used to monitor the light transmission during the thermal analysis. In a typical analysis, the
121 laser transmittance signals first decreases due to the pyrolysis of OC, then it increases as the
122 pyrolyzed OC is oxidized in the presence of O_2 . When the laser signal returns to its initial
123 value at the beginning of the analysis, this sets the split point differentiating OC and EC.

124 Ultra-high purity grade gases (He, 10% O_2 in He and 5% CH_4 in He) were used. An O_2 trap
125 (SGT Middelburg V. V., the Netherlands) was installed in the He gas line to remove trace
126 amounts of O_2 . The quartz fiber filters were pre-baked inside the main oven of the instrument
127 at 870°C for about 5 min before sample collection and were replaced weekly.

128 In addition, hourly data including PM_{2.5} mass, NO, NO₂, and O₃ at the sampling site are
129 provided by the Hong Kong Environmental Protection Department (HKEPD).

130 **2.2 Quality control and data validation**

131 The semi-continuous carbon analyzer collected samples approximately 90% of the time
132 between May 1, 2011 and April 30, 2012. No data were collected during June 21–July 20,
133 2011 due to instrument maintenance and during August 23–30, 2011 due to malfunctioning
134 of NDIR.

135 The analyzer computer was closely monitored through a secured phone line and the
136 instrument was checked daily for any error flags for hardware or software problems. Weekly
137 routine instrument maintenance includes sample filter replacement, cyclone cleaning, one-
138 point external calibration, gas-flow and instrument blank checking. The instrument blank for
139 total carbon (TC) during the study period ranged from 0.02 to 0.25 µgC, with an average of
140 0.13 µgC. For the 1-hr measurement (46-min sampling at a flow rate of 8 L/min), the blank
141 values translate to 0.05–0.66 µgC/m³ (average of 0.35 µgC/m³) in atmospheric concentrations.
142 The method detection limits (MDLs), determined to be three times the blank standard
143 deviation, were 0.60µgC/m³ for OC and 0.20 µgC/m³ for EC. Multi-point external
144 calibrations using known sucrose concentrations spiked on a prebaked filter were conducted
145 once every 1–2 months. Recommended by the manufacturer, 21.03 µgC was used for one
146 point calibration while 4.21, 21.03 and 42.07 µgC were used for multi-point calibration. The
147 recoveries of these three sucrose standard solutions were 119.0±8.4, 100.7±6.0 and
148 95.3±7.1%, respectively. When the organic denuder was changed once every two months, the
149 sampling flow rate calibration was performed and the actual flow rates were recorded within
150 8.0±0.4 L/min. Several experiments were conducted to determine the dynamic blank by
151 placing a 47-mm Teflon filter upstream of the denuder and sampling particle-free ambient air
152 into the analyzer on a 2-h collection/analysis cycle. The dynamic blank was in the range of
153 0.46–0.83 µgC/m³ with an average of 0.68 µgC/m³. The average dynamic blank corresponds
154 to 8.7% of the measured annual mean OC value. This value is consistent with the results from
155 previous studies (e.g. Polidori et al., 2006; Kang et al., 2010) and the finding from Turpin et
156 al. (1994) that the adsorption artifact is dependent on the concentrations of gaseous
157 OC/particulate OC. The volatilization of particulate OC from the sampling quartz fiber filter
158 was estimated to be 10±6% (upper limit) (Polidori et al., 2006). Considering that the positive
159 and negative artifacts are of comparable magnitude, no correction was made to the measured

160 OC concentrations in this study. The results from dynamic blank test serve as an estimate of
161 adsorption effect.

162 The data validation processes include checking of sampling volume, calibration peak area,
163 NDIR signals, and OCEC split point. Data with a sampled volume variation beyond the
164 tolerance of 5% (i.e., 368 ± 18 L) or a calibration peak area variation beyond the tolerance of
165 10% were considered to be invalid and excluded from the dataset. The raw data files of all the
166 collected samples were manually inspected to identify any abnormal OCEC split (i.e. the time
167 when the laser signal return to its initial value after the pyrolysis). In case of abnormal split,
168 the calculation software of the instrument was then used to process the raw data files with the
169 split point set manually. The data valid rate for the entire sampling period is 96%. The
170 effective sampling duration, data capture rates and valid rates for individual month are listed
171 in Table S2 in the supplementary material.

172 The semi-continuous OC and EC measurements (also abbreviated as RT measurements for
173 ease of discussion) were further validated by comparing with OC and EC data obtained from
174 two sets of off-line filter-based measurements. One is from the Hong Kong PM_{2.5} speciation
175 network program. In the speciation monitoring program, PM_{2.5} samples were collected on
176 prebaked 47-mm quartz fiber filters over a 24-h (starting from 0:00 at midnight) period by a
177 Partisol sampler (Rupprecht & Patachnick, Model 2025, NY, USA). The 24-h filter-based
178 measurements using the Partisol samplers, abbreviated as Partisol-TC, Partisol-OC and
179 Partisol-EC hereafter, were made every 6th day throughout the year. The other one is from the
180 PM_{2.5} organic speciation project. PM_{2.5} samples were collected on prebaked 20 × 25 cm
181 quartz fiber filters over a 24-h (starting from 0:00 at midnight) period by a High-Volume (HV)
182 PM_{2.5} particulate sampler (Tisch Environmental Inc., OH, USA) at a frequency of once every
183 three days. The HV sampler-derived measurements were abbreviated as HV-TC, HV-OC and
184 HV-EC hereafter. The sampled filters from both projects were stored in a freezer below –
185 20°C after collection and were analyzed using a lab-based thermal/optical carbon analyzer
186 (Sunset Laboratory, OR, USA). The ACE-Asia protocol (Schauer et al., 2003), a variant of
187 NIOSH protocol (Wu et al., 2012), was used for these 24-h filter samples. The hourly OC and
188 EC concentrations were averaged over the same 24-h period for comparison with the filter-
189 based concentrations. The comparisons are shown in Fig. 1.

190 The differences between the measurements were evaluated by zero-intercept linear regression,
191 average percent relative bias ($\% \overline{RB}$) and average percent relative standard deviation ($\% \overline{RSD}$).
192 The equations to calculate these two parameters are given in Appendix 1 in the

193 supplementary material. The instrument blanks for both the bench-top aerosol carbon
194 analyzer and the field OC-EC analyzer were statistically not different from zero after
195 considering the analytical and instrumental uncertainties of the blank. Hence, the zero-
196 intercept linear regression analysis was applied in the comparisons of the datasets.

197 TC by the semi-continuous method agrees reasonably well with both Partisol filter
198 measurements ($R^2 = 0.98$, $\% \overline{RB} = -29.6\%$, $\% \overline{RSD} = 23.4\%$) and high-volume filter
199 measurements ($R^2 = 0.99$, $\% \overline{RB} = -16.4\%$, $\% \overline{RSD} = 15.2\%$). Good correlations and
200 reasonable agreement were also observed for OC ($R^2 = 0.97$, $\% \overline{RB} = -33.8\%$, $\% \overline{RSD} = 27.7\%$
201 for RT-OC vs. Partisol-OC and $R^2 = 0.98$, $\% \overline{RB} = -17.9\%$, $\% \overline{RSD} = 18.4\%$ for RT-OC vs.
202 HV-OC). The average Y/X ratios were 0.75 ± 0.11 for RT-TC vs. Partisol-TC and 0.86 ± 0.11
203 for RT-TC vs. HV-TC, respectively. The Y/X ratios for RT-OC vs. Partisol-OC and RT-OC
204 vs. HV-OC were 0.72 ± 0.14 and 0.85 ± 0.18 , respectively. These numbers suggest that in
205 general both the TC and OC measurements from the off-line filter samples were larger than
206 those observed by the semi-continuous method. More specifically, the discrepancies were
207 larger between RT data and Partisol data than those between RT data and HV data. In
208 addition to the uncertainties associated with the sampling and analysis processes, another
209 possible reason is the positive artifacts due to organic vapor adsorption on the quartz fiber
210 filters since no denuder was used in either the Partisol or HV samplers. The amount of OC
211 adsorbed onto the quartz fiber filter in the Partisol samplers was expected to be higher than
212 that in the HV samplers as the face velocity of the Partisol sampler is approximately half of
213 that of the HV sampler (McDow et al., 1990).

214 The EC data comparisons show a higher degree of scatter than TC and OC ($R^2 = 0.93$ for RT-
215 EC vs. Partisol-EC and $R^2 = 0.86$ for RT-EC vs. HV-EC) while the average Y/X ratios for EC
216 suggested that the semi-continuous data agree better with the filter-based measurements
217 (0.88 ± 0.26 for RT vs. Partisol samples and 1.04 ± 0.38 for RT vs. HV samples, respectively).
218 Several studies reported poor agreement between thermal EC from the field analyzer and
219 those filter-based EC measurements due to high detection limit and differences in the
220 temperature programs (e.g. Schauer et al., 2003; Bae et al., 2004; Venkatachari et al., 2006).
221 However, the discrepancies between RT-EC and filter-based EC measured at roadside in this
222 study might also be attributed to the different sampling durations. The field analyzer collected
223 $PM_{2.5}$ samples for a total of 1104 minutes on a daily basis, accounting for about 3/4 of the 24-
224 h period. The sampled air by the RT-OCEC analyzer might not be able to fully represent the

225 24-h integrated sampling period by the filter-based measurements because of the high carbon
226 concentrations with large variations at MK.

227

228 **3 Results and Discussions**

229 **3.1 Organic and elemental carbon concentrations**

230 The annual average OC and EC concentrations at MK AQMS during the study period were
231 7.8 and 4.4 $\mu\text{gC}/\text{m}^3$, respectively. The average OC and EC concentrations in individual
232 months and in different seasons during the study period are shown in Fig. 2. Based on the
233 local meteorological characteristics, the seasons were defined as follows: March 16–May 15
234 as spring; May 16–September 15 as summer; September 16–November 15 as fall and
235 November 16–March 15 of the next year as winter (Chin, 1986; Yuan et al., 2006).

236 OC had clear seasonal variation, with higher values in the winter months (Nov–Feb) and the
237 lowest values recorded in summertime (Jun–Aug). In comparison, EC exhibited little
238 seasonal variations, suggesting that it dominantly came from local emission sources. The
239 relative contributions of OC to $\text{PM}_{2.5}$ ranged from 15.5% (Jul. 2011) to 29.3% (Jan. and Feb.
240 2012) while EC percent contribution to $\text{PM}_{2.5}$ mass was the highest in summer (17.7% in Jun.
241 2011) and lowest in winter (9.2% in Dec. 2011). This can be explained by the quite
242 comparable EC concentrations throughout the year while $\text{PM}_{2.5}$ concentrations much lower
243 during summertime than wintertime.

244 The weekly patterns showed that EC was elevated on weekdays and decreased to a minimum
245 on Sundays for all the months. OC also had the lowest values on Sundays compared to the
246 rest of the week but the variations were less distinct than those of EC. These patterns were
247 consistent with the traffic flow variation within a week and confirm vehicular sources as the
248 dominant contributor to EC while an important source for OC. For OC, unlike the EC
249 concentrations which maintained at a stable level during the study period, its concentrations
250 were evidently higher in winter months. This indicates the prominent influence of air
251 pollutants transported into the MK area from elsewhere.

252 The diurnal variations of carbon concentrations for weekdays (Mon–Fri), Saturdays, and
253 holidays (Sunday and public holidays) were examined for individual months (Fig. S1 & Fig.
254 S2) and four months were selected to represent the different seasons (Figures 3, August for
255 summer, October for fall, January for winter and March for spring). The difference of OC

256 concentrations between weekdays and holidays were more significant in summer than the
257 other seasons. In summer, air pollution transported from outside Hong Kong was much
258 reduced. OC observed in the sampling area was dominated by local sources such as vehicular
259 exhaust, cooking, etc. These activities were reduced on holidays (e.g. reduced bus schedule),
260 leading to lower OC concentrations. In winter and the two transitional seasons, on the other
261 hand, the air pollutants transported from elsewhere outside Hong Kong made a significant
262 contribution, weakening the influence of local emission sources on ambient OC
263 concentrations. Different from the variation patterns of OC, EC was always lower during
264 holidays, indicating the “local” characteristics of its major sources.

265 The diurnal profiles for OC and EC also differ. EC concentrations started to increase from
266 7:00 in the morning and two peaks (7:00–11:00 and 16:00–19:00) were observed during the
267 day. These two periods of higher EC coincided with the rush hours in the city. EC
268 concentrations started to decrease around 19:00, and remained at a relatively low level from
269 midnight till the next early morning. NO_x and EC were found to correlate quite well with
270 each other especially during the time period of 9:00 pm–6:00 am (the next day) and the first
271 rush hour period (Fig. 4). In these two periods, the emission sources at roadside were
272 relatively limited and EC and NO_x would be primarily from vehicular exhaust. In contrast,
273 during the rest of the day, various emission sources for NO_x , together with the higher
274 reactivity of NO_x during daytime, could lead to a weaker correlation between NO_x and EC
275 concentrations.

276 The OC concentrations also peaked twice a day (11:00–16:00 and 19:00–22:00). The diurnal
277 profile comparison between OC and O_3 showed that one O_3 peak commonly appeared in the
278 early afternoon but was about 1–2 h earlier than the afternoon OC peak (Fig. 5). In the
279 roadside environment, the ozone concentration level was much lower due to titration by NO.
280 Nevertheless, an ozone peak appearing in the early afternoon was consistently observed in
281 different seasons (Fig. 5). Such a temporal characteristic tends to indicate that ozone could be
282 an indicator of photochemical processes even in a high NO roadside environment. In view of
283 the consistent observation of an ozone peak in the early afternoon, it is possible that the first
284 OC peak was related to secondary organic aerosol (SOA) formation. The nighttime OC peak,
285 on the other hand, could be associated with emissions from the larger number of mainly
286 gasoline-fuelled private cars on the road. In addition, the cooking-related activities possibly
287 also contribute to the higher OC levels during both of the time periods.

288 The different diurnal variations of OC and EC concentrations result in an OC/EC ratio pattern
289 of three peaks appearing during the day (Fig. S3). The first one is observed in the early
290 morning when EC concentrations were much lower than those of OC. The second peak
291 appeared in the early afternoon, coinciding with the first OC peak. The third peak was at
292 around 20:00 in the evening when the OC concentrations were high while EC concentrations
293 started to decrease.

294 **3.2 Estimation of the $(OC/EC)_{\text{vehicle}}$**

295 The EC-tracer method, due to its simplicity, has long been used to estimate the relative
296 contributions of primary and secondary sources to measured particulate OC (e.g. Chu and
297 Macias, 1981; Wolff et al., 1982; Turpin et al., 1991; Turpin and Huntzicker, 1995; Cabada et
298 al., 2004; Plaza et al., 2006; Lonati et al., 2007; Yu et al., 2009). This method is based on the
299 assumption that EC is exclusively primary in origin and that EC and primary OC have
300 common emission sources (e.g. combustion, resuspension of combustion particles, etc.). The
301 measured OC concentration is the sum of POC and SOC:

$$302 \quad [OC]_{\text{measured}} = \text{POC} + \text{SOC} \quad (1)$$

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

$$305 \quad \text{POC} = [OC]_{\text{combustion}} + b \quad (2)$$

306 where b denotes non-combustion primary OC.

307 If an $(OC/EC)_{\text{pri}}$ representing the primary combustion sources at the measurement site is
308 known, POC can be calculated using the equation below:

$$309 \quad \text{POC} = \text{EC} \times (OC/EC)_{\text{pri}} + b \quad (3)$$

310 SOC can be subsequently derived as the difference between $[OC]_{\text{measured}}$ and POC, i.e., Eq (4).

$$311 \quad \text{SOC} = [OC]_{\text{measured}} - [\text{EC} \times (OC/EC)_{\text{pri}} + b] \quad (4)$$

312 Several approaches have been reported in the literature to estimate the $(OC/EC)_{\text{pri}}$, including
313 the use of (1) emission inventories of OC and EC from primary sources (*Gray et al.*, 1986);
314 (2) ambient OC and EC measurements made when primary source emissions are dominant
315 or/and when photochemical activities are weak (Turpin and Huntzicker, 1991); and (3) the
316 minimum OC/EC ratio obtained in the study period (Lim and Turpin, 2002). It is not a trivial
317 task to ensure that $(OC/EC)_{\text{pri}}$ determined in these approaches is representative of the

318 composite effect of multiple primary combustion sources, each having a time-varying
 319 contribution to the ambient OC and EC. In addition, uncertainty in estimating b (see
 320 discussion later in this section) introduces additional uncertainty in the estimates of POC and
 321 SOC. While we recognize the difficulty in deriving reliable POC and SOC concentrations, by
 322 comparison we see it is a much simpler task to derive an $(OC/EC)_{\text{vehicle}}$ ratio representative of
 323 vehicular emissions for our roadside environment, since it has the unique characteristic of
 324 vehicular emissions being the dominant EC source. Once $(OC/EC)_{\text{vehicle}}$ is determined,
 325 OC_{vehicle} can be calculated using eq (5):

$$326 \quad OC_{\text{vehicle}} = EC \times (OC/EC)_{\text{vehicle}} \quad (5)$$

327 The approaches we use here in estimating $(OC/EC)_{\text{vehicle}}$ are the same as the last two
 328 approaches described above for $(OC/EC)_{\text{pri}}$. We first use a subset of data that have a given
 329 percentage of the lowest OC/EC ratios among the complete data set to derive $(OC/EC)_{\text{min}}$
 330 (Castro et al., 1999). The slope ($(OC/EC)_{\text{min}}$) and the intercept (b) in eq (3) were calculated
 331 by Deming regression of OC on EC using the lowest 5% data by OC-to-EC ratio. In the
 332 Deming regression analysis, the uncertainties in both x- and y-axes are taken into account
 333 (Deming, 1943; Cornbleet and Gochman, 1979). Deming regression has been shown to have
 334 better performance in the EC tracer method than the ordinary least-square (OLS) regression,
 335 which only considers random measurement errors in y (Chu et al., 2005; Saylor et al., 2006).

336 There are different forms of Deming regression because of different ways of representing
 337 measurement errors in x and y , i.e. $\omega(X_i)$ and $\omega(Y_i)$ in eq (6) for S , which is the sum of the
 338 square of the perpendicular distances between the data points and the regression line (Saylor
 339 et al., 2006).

$$340 \quad S = \sum[\omega(X_i)(x_i - X_i)^2 + \omega(Y_i)(y_i - Y_i)^2] \quad (6)$$

341 In eq (6), X_i and Y_i are the observed data points and x_i and y_i are the adjusted points lying on
 342 the regression line. The simplest form of Deming regression, termed default Deming
 343 regression, adopts a value of 1 for λ , the ratio of $\omega(X_i)$ and $\omega(Y_i)$ (eq (7)). In another words,
 344 equal measurement uncertainties for variable X_i and Y_i are assumed.

$$345 \quad \lambda = \omega(X_i)/\omega(Y_i) \quad (7)$$

346 Saylor et al. (2006) compared two forms of Deming regression, default Deming regression
 347 with $\lambda = 1$ and optimal Deming regression with an accurate representation of
 348 λ (i.e., $\lambda = \text{Var}(\varepsilon_{OC})/\text{Var}(\varepsilon_{EC})$, where $\text{Var}(\varepsilon)$ is the variance of the measurement errors,

349 ϵ). Using simulated EC and OC data, they demonstrated that the optimal Deming regression
350 provides excellent results while the default Deming regression yields a slope of 6% larger
351 than the true value and a negative intercept of -1.28 due to inaccurate representation of error
352 variance. We therefore adopt optimal Deming regression in our linear regression approach to
353 calculate $(OC/EC)_{\min}$, and λ is taken to be the ratio of the measurement error variance of X
354 and Y .

355 The regressions were performed on a monthly, seasonal and annual basis so as to evaluate the
356 robustness of different subsets of data and the results are shown in Table 1. It is noted that
357 some intercept values are negative, which does not seem to have a physical basis. To
358 understand the issue of negative intercepts, we next examine regression lines obtained with
359 OLS, default Deming, and optimal Deming regression for the January 2012 data (Fig. S4),
360 which had the largest negative intercept (-0.58) among all the monthly $(OC/EC)_{\min}$. The OLS
361 regression results in a positive intercept (0.86) while the two Deming regressions give
362 negative intercepts. The different regression lines are apparently a result of difference in
363 assigning weights to individual observations. This result suggests that the regression line
364 intercept is fairly sensitive to weights assigned to individual observations, or in another word,
365 error variances for X and Y variables. For actual ambient data, it is difficult to identify a
366 subset of data that is free of SOC contribution or such a subset of data simply does not exist.
367 In addition, multiple primary combustion sources that have different $(OC/EC)_{\text{pri}}$ co-exist and
368 their relative strengths vary with time at a given ambient location. Both factors would
369 contribute to scattering of the data that are used for deriving $(OC/EC)_{\text{pri}}$, which in turn could
370 lead to a negative intercept, as illustrated by Fig. S4. This analysis about intercept shows the
371 large uncertainty associated with the estimated b when using linear regression approaches.
372 One needs to be cautious in estimating POC and SOC if a linear regression approach is relied
373 upon for the calculation of non-combustion-derived primary OC (i.e., b in eqs. (3) and (4)).
374 On the other hand, we note the slope is much less sensitive to different regression approaches.
375 In the example of the January 2012 data, the slope values derived from the two Deming
376 regressions differ less than 5% (Fig. S4). This adds to our confidence in the robustness of the
377 derived $(OC/EC)_{\min}$ using Deming regression of select ambient OC and EC data.

378 The monthly $(OC/EC)_{\min}$ values derived using the lowest 5% data by OC-to-EC ratio
379 exhibited lower values during summer months. In particular, the value was 0.38 in July and
380 0.52 in August. Higher values of $(OC/EC)_{\min}$ were observed for December 2011 (1.46) and
381 January 2012 (1.42). The monthly variations of $(OC/EC)_{\min}$ are consistent with the

382 estimations for different seasons. The lowest value (0.49) was found in summer, which is a
383 season mainly under the influence of local primary emissions and from time to time the
384 southerly winds from the ocean would bring in cleaner air to further dilute the pollution in
385 Hong Kong. During winter season, the prevailing winds were northerly and northeasterly and
386 the regional transport of air pollutants played a significant role (Yu et al., 2004). The higher
387 $(OC/EC)_{\min}$ ratio is a combined result of primary sources having higher (OC/EC) and non-
388 negligible contribution of SOA in the 5% lowest (OC/EC) samples. Spring and fall are
389 transitional seasons with prevailing winds as a combination of southerly and northerly and
390 therefore the $(OC/EC)_{\min}$ values were recorded to be in-between.

391 Since local primary emission sources are dominant during summertime, additional Deming
392 regressions were performed on the summer OC and EC dataset by varying the percentage of
393 included data from the lowest 5% to 100% (Table 2). The regression slope gradually
394 increases from 0.49 when the lowest 5% data ($n = 94$) are used for regression to 1.21 as all
395 summer data ($n = 1878$) are included for regression. The summer data and the Deming
396 regression lines are shown in Fig. S5. Based on this Deming regression analysis for this
397 “local emissions-influenced” period, a value of 0.5 was suggested to approximate
398 $(OC/EC)_{\text{vehicle}}$ while 1.2 could serve as an upper limit of $(OC/EC)_{\text{vehicle}}$ estimate at this
399 roadside site.

400 To evaluate the impact of different emission sources on the OC/EC ratio, we further
401 examined the OC/EC ratios in subsets of data selected according to the carbon diurnal
402 profiles. Three time periods were chosen; including two EC peak times (7:00–11:00 in the
403 morning and 16:00–19:00 in the afternoon) and one OC peak time (19:00–22:00 in the
404 evening). The appearance of EC peaks in the daytime and OC peak in the evening time
405 reflected enhancement of primary emissions during these periods. Hence, the OC/EC ratios in
406 these time periods were more influenced by primary emissions. Table 3 lists the average
407 OC/EC ratios, calculated as the average OC to the average EC, in the three time periods in
408 individual months. We note that data from the identified episodic periods, defined to be
409 periods when the hourly $PM_{2.5}$ mass concentrations exceeded the monthly average plus one
410 standard deviation for 4 hours or more, were excluded since on episode days the carbon
411 concentrations were considerably influenced by more aged air masses transported from
412 outside-Hong Kong.

413 The average OC/EC ratio for the same time period varied with months. Higher values were
414 observed in fall and winter months while lower in summer months (May–September). This is

415 consistent with the hypothesis that local sources dominated in summertime while transported
416 air masses largely impacted Hong Kong during winter leading to higher OC/EC ratios.

417 Within the same month, the OC/EC ratios in the two EC peak periods were mostly
418 comparable and 4-40% higher in the second EC peak periods, and both periods were lower
419 than that in the period of 19:00–22:00. This is expected since the first two periods were
420 dominated by vehicular emissions. During these two rush-hour periods of the day, public
421 transportation (e.g. buses, light buses, good vehicles, etc.) were predominant on the road and
422 most of them were diesel-powered vehicles. During evening time, more private cars, which
423 were predominately powered by gasoline engines, were on the road. The OC/EC ratios, as
424 reported in source profile studies, were 0.6–0.8 for diesel engine exhaust, 2.2–4.2 for
425 catalyst-equipped gasoline exhaust, and 8.2–60.0 for noncatalyst gasoline-powered exhaust
426 (Hildemann *et al.*, 1991; Schauer *et al.*, 1999a, 2002a). The compositional variation in the on-
427 road motor vehicles is expected to result in different OC/EC ratios. The average OC/EC
428 ratios in the 19:00-22:00 were 46-82% higher than those in the 16:00-19:00 periods in
429 different months. The elevation of OC relative to EC in the 19:00-22:00 could not possibly
430 come from SOC, as the SOC contribution would be expected be higher in the 16:00-19:00
431 period which was partly daytime. In view of the site in a district of numerous restaurants, the
432 consistently higher OC/EC during 19:00–22:00 was most likely caused by cooking-related
433 activities. Work on cooking source samples revealed that little EC was emitted from cooking
434 while OC accounted for 34–69% of the emitted PM_{2.5} mass (Hildemann *et al.*, 1991; Schauer
435 *et al.*, 1999b, 2002b). This primary OC source from cooking would certainly increase the
436 ambient OC/EC ratios.

437 The comparisons between the calculated $(OC/EC)_{\min}$ values using all data versus the average
438 OC/EC in subsets of the data under significant influence of primary emissions clearly show
439 the difficulty in deriving a single $(OC/EC)_{\text{pri}}$ value to represent a composite of multiple
440 primary sources, since each source makes time-varying contributions. It can also be seen that
441 using the $(OC/EC)_{\min}$ to represent the primary OC/EC ratio in the EC-tracer method would
442 lead to overestimation of SOC during time periods when cooking-related sources were
443 significant. Partly for this reason, we did not attempt to estimate POC and SOC in this study.
444 On the other hand, the accumulative evidence suggests that it is reasonable to adopt a value
445 of 0.5, the $(OC/EC)_{\min}$ value derived from Deming regression of the 5% lowest summer data
446 by OC-to-EC ratio, to approximate the OC/EC ratio for vehicular emissions. With EC at this
447 location is predominantly from vehicular emissions, the vehicle-related OC (i.e., OC_{vehicle}) is

448 then $0.5 \times \text{EC}$. We note $\text{OC}_{\text{vehicle}}$ estimated in this way only accounts for primary OC
449 emission from vehicles. SOC formed from volatile organic compound (VOC) precursors
450 emitted by vehicles (e.g., toluene) is not captured in this EC tracer approach.

451 **3.3 Estimation of vehicle-related OC and $\text{PM}_{2.5}$**

452 **3.3.1 Estimation using $(\text{OC}/\text{EC})_{\text{vehicle}}$ inferred from OCEC measurements**

453 The annual average vehicle-related OC ($\text{OC}_{\text{vehicle}}$) concentration was $2.2 \pm 1.2 \mu\text{gC}/\text{m}^3$, which
454 represents $32.0 \pm 18.9\%$ of the annual average particulate OC. The monthly average $\text{OC}_{\text{vehicle}}$
455 concentrations showed little variation throughout the year ($1.9\text{--}2.4 \mu\text{gC}/\text{m}^3$) while the percent
456 contribution to total OC varied from 16.6% in December to 64.0% in July. By applying a
457 ratio of 1.4 to convert OC to organic matter (OM) (Malm et al., 1994), the daily-average
458 contributions of vehicle-related organic aerosols ($\text{OM}_{\text{vehicle}}$) to the $\text{PM}_{2.5}$ mass were estimated
459 to be in the range of 3.5–24.8%. By further summing up the concentrations of $\text{OM}_{\text{vehicle}}$ and
460 EC, the vehicle-related carbonaceous $\text{PM}_{2.5}$ ($\text{PM}_{\text{vehicle}}$) and its contributions to the $\text{PM}_{2.5}$ mass
461 can be estimated. The monthly average $\text{PM}_{\text{vehicle}}$ ranged from 6.5 to $8.3 \mu\text{gC}/\text{m}^3$ and exhibited
462 little seasonal variations (Fig. 6), reflecting the local nature of vehicular emission source. Its
463 relative contributions to the total $\text{PM}_{2.5}$ mass, on the other hand, varied from 16.0% (Dec.
464 2011) to 35.6% (Aug. 2011) with an annual average of 24.8%. The percent contribution
465 differences were mainly due to higher $\text{PM}_{2.5}$ levels during winter time. Calculations also
466 show that the average $\text{PM}_{\text{vehicle}}$ concentrations were estimated to be $10.3 \mu\text{g}/\text{m}^3$ during the
467 first rush hour period (7:00–11:00) on non-holidays and $6.5 \mu\text{g}/\text{m}^3$ for the same period on
468 holidays (including Sundays and public holidays). Hence, a reduction of approx. 37% in
469 $\text{PM}_{2.5}$ mass for the period of 7:00–11:00 on holidays could be attributed to reduction in
470 vehicular emissions, which is a result of reduced on-road public transportation (e.g. diesel-
471 powered buses). On Sundays and public holidays, bus frequencies decrease by 20–30%
472 compared to the rest of the week. These results indicate that the emissions from on-road
473 vehicles are an important source of $\text{PM}_{2.5}$ in the urban roadside environment of Hong Kong.

474 **3.3.2 Estimation using receptor modeling analysis**

475 The $\text{OC}_{\text{vehicle}}$ were also estimated by a receptor modeling approach so that comparisons can
476 be conducted for evaluation of the EC tracer method. In the receptor modeling approach,
477 source apportioning was performed on OC and EC by Positive Matrix Factorization (PMF)
478 Model. The input data consist of hourly concentrations of 27 volatile organic compounds

479 (VOCs), NO, NO₂, OC and EC. The VOC measurements were conducted on an hourly/half-
480 hourly basis using a GC955 series 611/811 VOC analyzer (Syntech Spectras, Netherlands) at
481 MK AQMS. Isoprene was excluded from the input dataset since the biogenic emissions at
482 roadside can be neglected. *Iso*-hexane was also excluded as >30% of its measurements were
483 below the method detection limit.

484 The uncertainties for individual species were initially estimated as $(s_{ij} + MDL_{ij}/3)$ (e.g.,
485 Polissar et al., 1998; Reff et al., 2007), where MDL_{ij} is the method detection limit and s_{ij} is
486 the analytical uncertainty of the corresponding species in the data set. The analytical
487 uncertainties were assumed to be 10% of the species concentrations for most of the VOCs
488 and 5% for NO and NO₂. The smaller molecules (i.e. ethane, ethane and ethyne) coelute in
489 the GC analysis, causing larger uncertainties. A few VOCs (e.g. 1,3,5- and 1,2,3-
490 trimethylbenzenes, butenes and pentenes) were detected in less than 90% of the samples. The
491 uncertainties of these VOCs were increased by a factor of 3 in the PMF analysis. For data
492 which are below the detection limits, the concentrations were replaced with the value
493 $(MDL_{ij}/2)$ and the corresponding uncertainty was set to $((5/6) \times MDL_{ij})$ (Polissar et al., 1998).

494 The source apportioning modeling was performed using EPA PMF 3.0 software (available at
495 <http://www.epa.gov/heads/research/pmf.html>). This software provides the bootstrap model
496 which is based on the Monte Carlo principle to check the mathematical stability of selected
497 runs (Norris et al., 2008). Each modeling run included 20 base runs and the base run with the
498 minimum Q value was retained as the solution. Solutions for 4–9 factors were tested and the
499 six-factor solution was considered to be the reasonable one. The source profiles of the six-
500 factor solution are shown in Fig. 7.

501 The first factor is rich in ethane, ethyne and benzene, all of which are relatively stable species.
502 This factor is therefore associated with aged air mass, which was transported from other
503 places. During the aging processes, reactive compounds such as alkenes would decay more
504 rapidly than unreactive species and the oxidative state of the aerosols would be increased.
505 The OC/EC ratio in this source profile was higher than 2, consistent with the nature of aged
506 air mass.

507 The second, third and sixth factors are all identified as vehicular emissions from diesel-
508 powered and gasoline-powered engines. Factor 2 is proposed to be dominated by diesel
509 exhaust as it is characterized by the presence of 1,3,5-trimethylbenzene, 1,2,4-
510 trimethylbenzene and 1,2,3-trimethylbenzene. The three VOC species appear in the distinct

511 source profile of Hong Kong diesel fuel, as reported by Tsai et al. (2006). In particular, this
512 factor is associated with the lowest OC/EC ratio (0.44) among all the factors, together with a
513 large amount of NO. These characteristics strongly suggest the association of this factor with
514 freshly emitted diesel exhaust. Factor 3 is dominated by *i*-pentane, *n*-pentane, pentenes and
515 three trimethylbenzenes. Since pentanes have been reported as markers of gasoline vapors in
516 Hong Kong (Tsai et al., 2006) and the OC/EC ratio in this factor (1.13) is higher than that in
517 factor 2, it is suggested that the third factor represents the better mixed air mass. Factor 6 is
518 related to gasoline-powered engine exhaust, characterized by the presence of *i*-pentane which
519 is the major component in gasoline vapor, and *cis*-2-butene and 1,3-butadiene which are two
520 common indicators for vehicle exhaust. The OC/EC ratio in this factor (2.36) is higher than
521 those in the other two factors.

522 The fourth factor is distinguished by a large amount of toluene, benzene, ethylbenzene,
523 xylenes, C₆ and C₇ alkanes. This source is considered to be a composite of emissions from
524 solvent use, architectural paints and industrial activities (Seila et al., 2001; Chan et al., 2006).
525 The industrial and architectural sources are an important source of aromatic VOCs, but they
526 make limited contributions to particulate OC and EC at MK.

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

532 On the basis of the source identifications, OC apportioned into factors 2, 3, 5 and 6 were
533 summed up to represent the PMF-derived OC_{vehicle}. The comparison of daily OC_{vehicle}
534 obtained from the EC-tracer method and the PMF approach is shown in a time series plot (Fig.
535 8). A fairly good agreement was observed between the estimations from the two methods (R^2
536 = 0.96). On average, PMF-derived OC_{vehicle} were approximately 25% higher than those
537 calculated by the EC-tracer method. The discrepancies could be due to one or a combination
538 of the following reasons: 1) uncertainties of the PMF analysis; 2) uncertainty in the
539 (OC/EC)_{vehicle} caused by the variation of the vehicle composition and 3) omission of the
540 cooking-related OC.

541 The relative contributions of different vehicular emission sources to the OC_{vehicle} and EC were
542 estimated by the PMF approach (Fig. 8, pie charts). The diesel-dominant factor (Factor 2)

543 contributed the most to EC and approximately one third to OC_{vehicle} . The gasoline-dominant
544 factor (Factor 6) contributed the least to EC but the most to OC_{vehicle} . These estimations
545 indicate that both diesel-powered and gasoline-powered vehicles are significant contributing
546 sources to the carbonaceous particle levels at roadside.

547

548 **4 Conclusions**

549 $PM_{2.5}$ carbon measurements of hourly time resolution were conducted in the roadside
550 environment of Hong Kong for the first time, over a 12-month period from May 2011 to
551 April 2012. Three levels of validation were performed and the data valid rate for the entire
552 sampling period is approximately 96%. The OC and EC concentrations at MK AQMS during
553 the study period were on average 7.8 and 4.4 $\mu\text{gC}/\text{m}^3$, respectively. Higher OC
554 concentrations were recorded during winter months as a result of the contributions of regional
555 air pollutant transport. EC concentrations were comparable among individual months. In
556 addition, the EC concentrations peaked in two time periods which coincided with the traffic
557 rush hours of a day. Both results indicate that EC was dominantly emitted from local
558 vehicular sources.

559 The minimum OC/EC ratios for periods of elevated EC were derived using Deming
560 regression. The results indicated that using a single value to represent $(OC/EC)_{\text{pri}}$ for the
561 purpose of estimating POC and SOC by the EC-tracer method may cause significant biases
562 since there were multiple significant primary emission sources in the sampling area, each
563 making time-varying contributions. On the other hand, a value of 0.5, mainly based on OC
564 and EC measurements in the lowest 5% by OC-to-EC ratio in the summer during which local
565 emissions dominated as a result of prevailing meteorological conditions, can be proposed to
566 reasonably approximate the OC/EC ratio for primary vehicular emissions. The annual
567 average vehicle-related OC concentration was subsequently estimated to be $2.2 \pm 1.2 \mu\text{gC}/\text{m}^3$,
568 which accounted for $32.0 \pm 18.9\%$ of the total $PM_{2.5}$ OC. The monthly average OC_{vehicle}
569 concentrations had a small variation throughout the year ($1.9\text{--}2.4 \mu\text{gC}/\text{m}^3$) while its
570 contribution to total OC varied from 16.6% (December 2011) to 64.0% (July 2011). The
571 OC_{vehicle} derived from source apportionment analysis by PMF are in good agreement with the
572 estimates using the proposed $(OC/EC)_{\text{vehicle}}$, adding confidence to the estimated primary OC
573 contribution from the vehicular source. Assuming an OM-to-OC ratio of 1.4, the daily-
574 average contributions of OM_{vehicle} to $PM_{2.5}$ ranged from 3.5 to 24.8%. The annual average
575 concentration of PM_{vehicle} was estimated to be $7.4 \mu\text{g}/\text{m}^3$ and accounted for approx. 25% of

576 the PM_{2.5} concentration, confirming vehicular emissions as an important source of PM_{2.5}
577 mass.

578 The carbon diurnal profiles also suggest cooking-related activities as an important primary
579 source to OC in the study area, making it difficult relying on the EC tracer method to estimate
580 the relative contributions of POC and SOC. Higher resolution measurements of particle-phase
581 tracer compounds for the cooking sources (e.g. C₁₆ and C₁₈ fatty acids) and for the vehicle-
582 related SOA (e.g., phthalic acid) in conjunction with receptor modeling could provide
583 possibilities in a more accurate estimation of SOA contributions in the urban areas of Hong
584 Kong.

585

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595

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Table 1. Deming regression results of $(OC/EC)_{\min}$ (the slope) and non-combustion term b (the intercept) using the lowest 5% data by OC-to-EC ratio on a monthly, seasonal and annual basis from the one-year carbon measurements at MK AQMS.

Time period	No. of data	λ (Y/X) ¹	$(OC/EC)_{\min}$ (slope) ²	Non-combustion term b (intercept) ²	Correlation coefficient (R^2)
May 2011	34	0.53	0.73 (± 0.025)	0.12 (± 0.190)	0.83
Jun. 2011	24	0.25	0.50 (± 0.035)	-0.29 (± 0.247)	0.64
Jul. 2011	12	0.15	0.38 (± 0.020)	0.18 (± 0.083)	0.95
Aug. 2011	24	0.27	0.52 (± 0.011)	-0.24 (± 0.051)	0.97
Sep. 2011	36	0.29	0.54 (± 0.018)	0.47 (± 0.121)	0.75
Oct. 2011	38	0.54	0.73 (± 0.017)	0.04 (± 0.097)	0.77
Nov. 2011	36	0.49	0.70 (± 0.032)	0.19 (± 0.184)	0.44
Dec. 2011	36	2.14	1.46 (± 0.025)	-0.18 (± 0.161)	0.90
Jan. 2012	38	2.01	1.42 (± 0.046)	-0.58 (± 0.325)	0.70
Feb. 2012	36	0.96	0.98 (± 0.029)	0.25 (± 0.207)	0.93
Mar. 2012	34	0.62	0.78 (± 0.023)	0.61 (± 0.155)	0.85
Apr. 2012	36	0.37	0.61 (± 0.008)	0.32 (± 0.048)	0.88
Summer	94	0.24	0.49 (± 0.003)	-0.20 (± 0.017)	0.90
Fall	72	0.45	0.67 (± 0.011)	0.05 (± 0.065)	0.73
Winter	142	1.02	1.01 (± 0.009)	-0.23 (± 0.062)	0.69
Spring	66	0.45	0.67 (± 0.020)	-0.15 (± 0.134)	0.63
Year	372	0.38	0.62 (± 0.002)	-0.23 (± 0.008)	0.80

¹ $\lambda = \text{Var}(\epsilon_{OC}) / \text{Var}(\epsilon_{EC})$, where $\text{Var}(\epsilon)$ is the variance of the measurement errors, ϵ .

² Values inside parentheses are 95% confidence interval.

Table 2. Deming regression results of $(OC/EC)_{min}$ using subsets of summer EC and OC data varying from the lowest 5% by OC-to-EC ratio to 100%.

Lowest % by OC/EC	No. of data	$(OC/EC)_{min}$ (slope) ¹	Non-combustion term b (intercept) ¹	Correlation coefficient (R ²)
5	94	0.49 (± 0.003)	-0.20 (± 0.017)	0.90
10	188	0.57 (± 0.003)	-0.26 (± 0.013)	0.86
20	376	0.66 (± 0.002)	-0.26 (± 0.009)	0.78
30	564	0.76 (± 0.002)	-0.38 (± 0.009)	0.72
40	752	0.81 (± 0.002)	-0.31 (± 0.007)	0.68
50	940	0.88 (± 0.001)	-0.32 (± 0.007)	0.63
60	1128	0.99 (± 0.002)	-0.54 (± 0.007)	0.59
70	1316	1.08 (± 0.002)	-0.67 (± 0.007)	0.55
80	1504	1.19 (± 0.002)	-0.80 (± 0.007)	0.50
90	1692	1.24 (± 0.002)	-0.67 (± 0.007)	0.50
100	1878	1.21 (± 0.002)	-0.19 (± 0.006)	0.33

¹ Values inside parentheses are 95% confidence interval.

Table 3. The average OC-to-EC ratios, calculated as ratio of average OC to average EC, in time periods of 7:00–11:00, 16:00–19:00 and 19:00–22:00 for individual months.

Month	Time period		
	7:00–11:00	16:00–19:00	19:00–22:00
May 2011	0.97	1.22	1.94
Jun. 2011	0.64	0.88	1.45
Jul. 2011	0.56	0.77	1.32
Aug. 2011	0.70	0.82	1.29
Sep. 2011	1.00	1.09	1.88
Oct. 2011	1.27	1.39	2.14
Nov. 2011	1.26	1.32	2.20
Dec. 2011	2.36	2.45	3.66
Jan. 2012	1.90	2.11	3.14
Feb. 2012	1.41	1.77	3.22
Mar. 2012	1.15	1.46	2.35
Apr. 2012	1.04	1.20	1.76

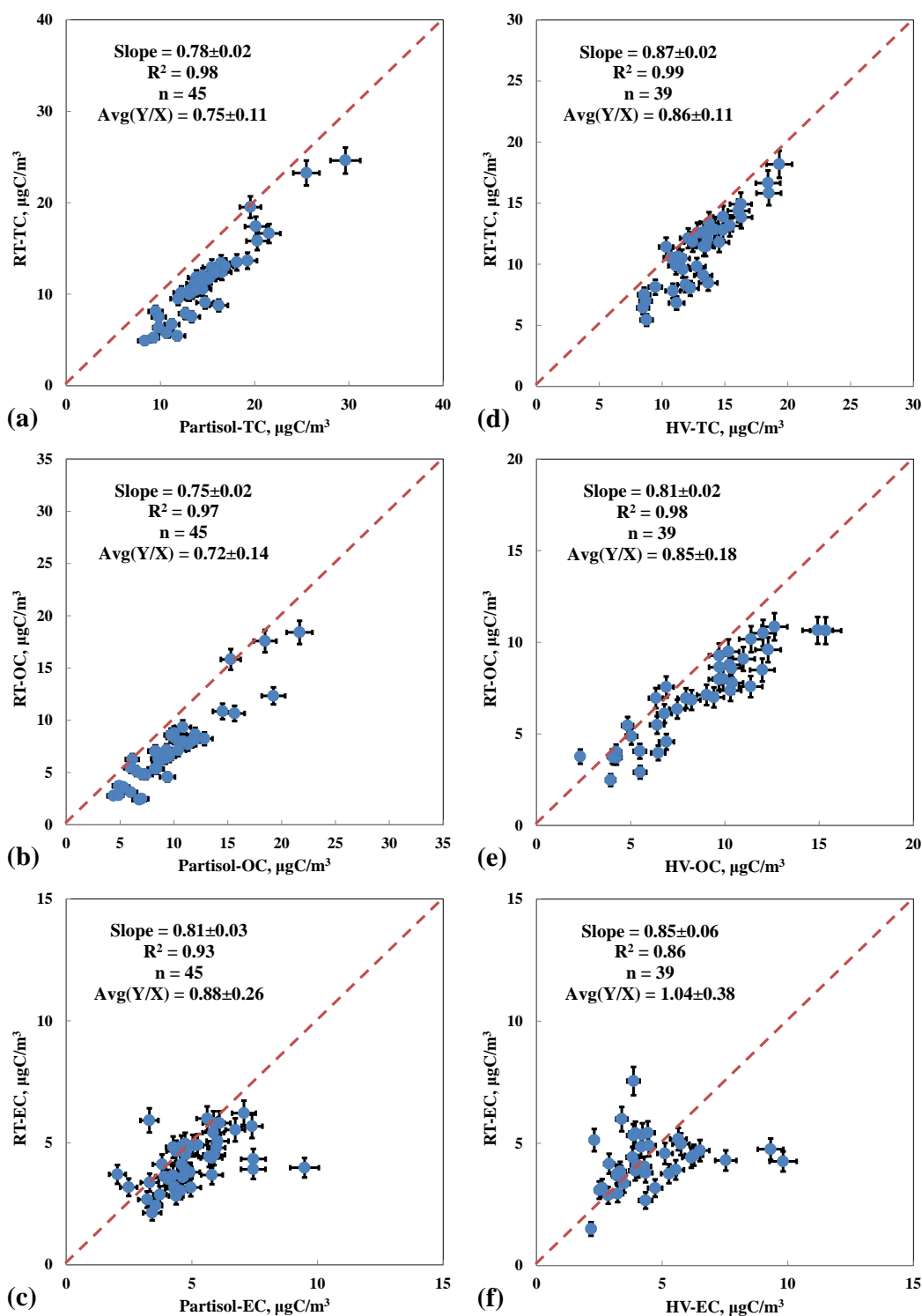


Figure 1. Scatter plots of semi-continuous measurements versus filter-based chemical data for $PM_{2.5}$ samples collected at MK AQMS during May 2011–April 2012. (a) RT-TC vs. Partisol-TC by TOT; (b) RT-OC vs. Partisol-OC by TOT; (c) RT-EC vs. Partisol-EC by TOT; (d) RT-TC vs. HV-TC by TOT; (e) RT-OC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

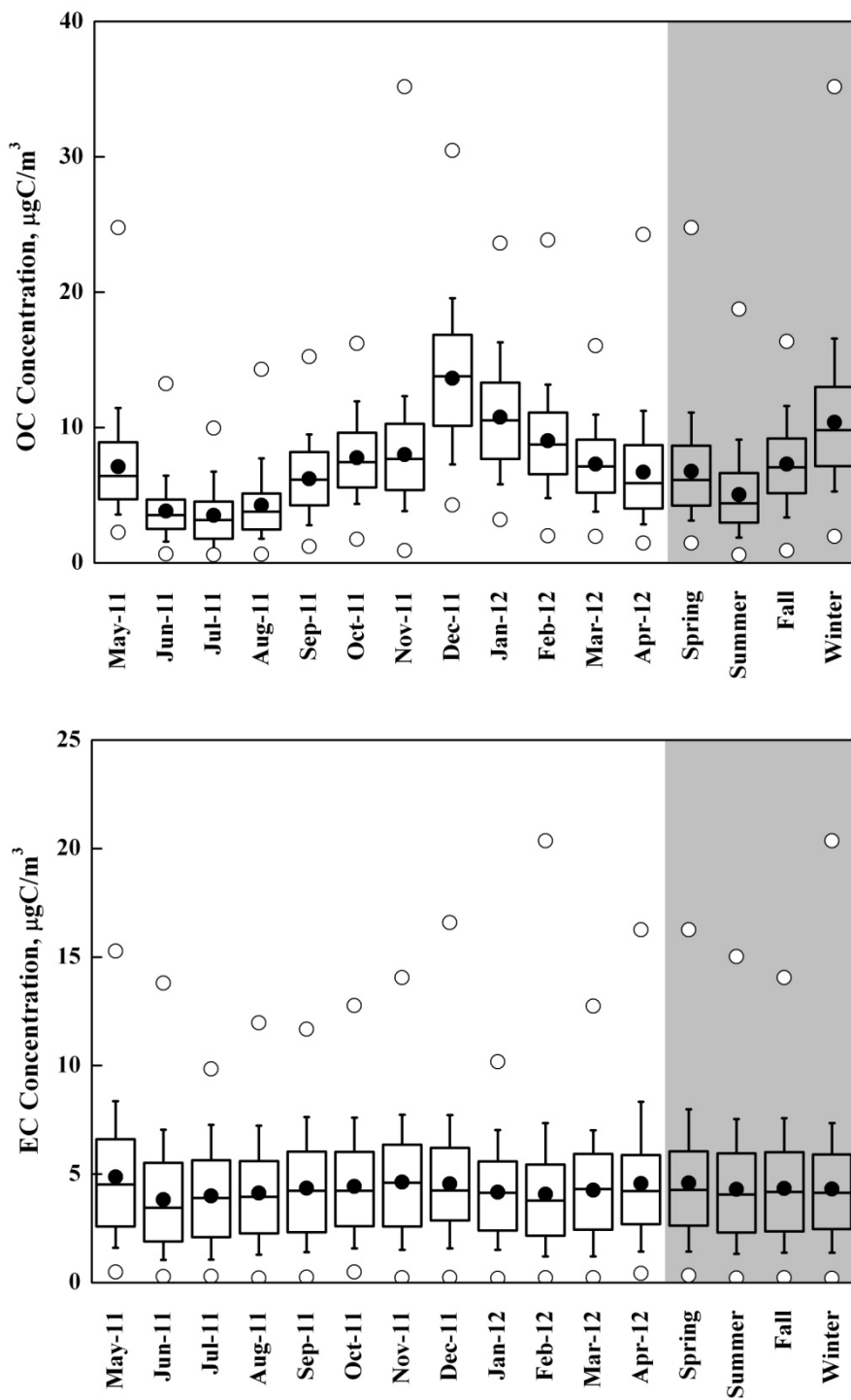


Figure 2. The 1-hr OC and EC concentrations in individual sampling months and in different seasons at MK AQMS during the study period from May 2011 to April 2012 (The box length: the 25th and the 75th percentiles; the whiskers: the 10th and the 90th percentiles; the dot in the box: the average; the line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

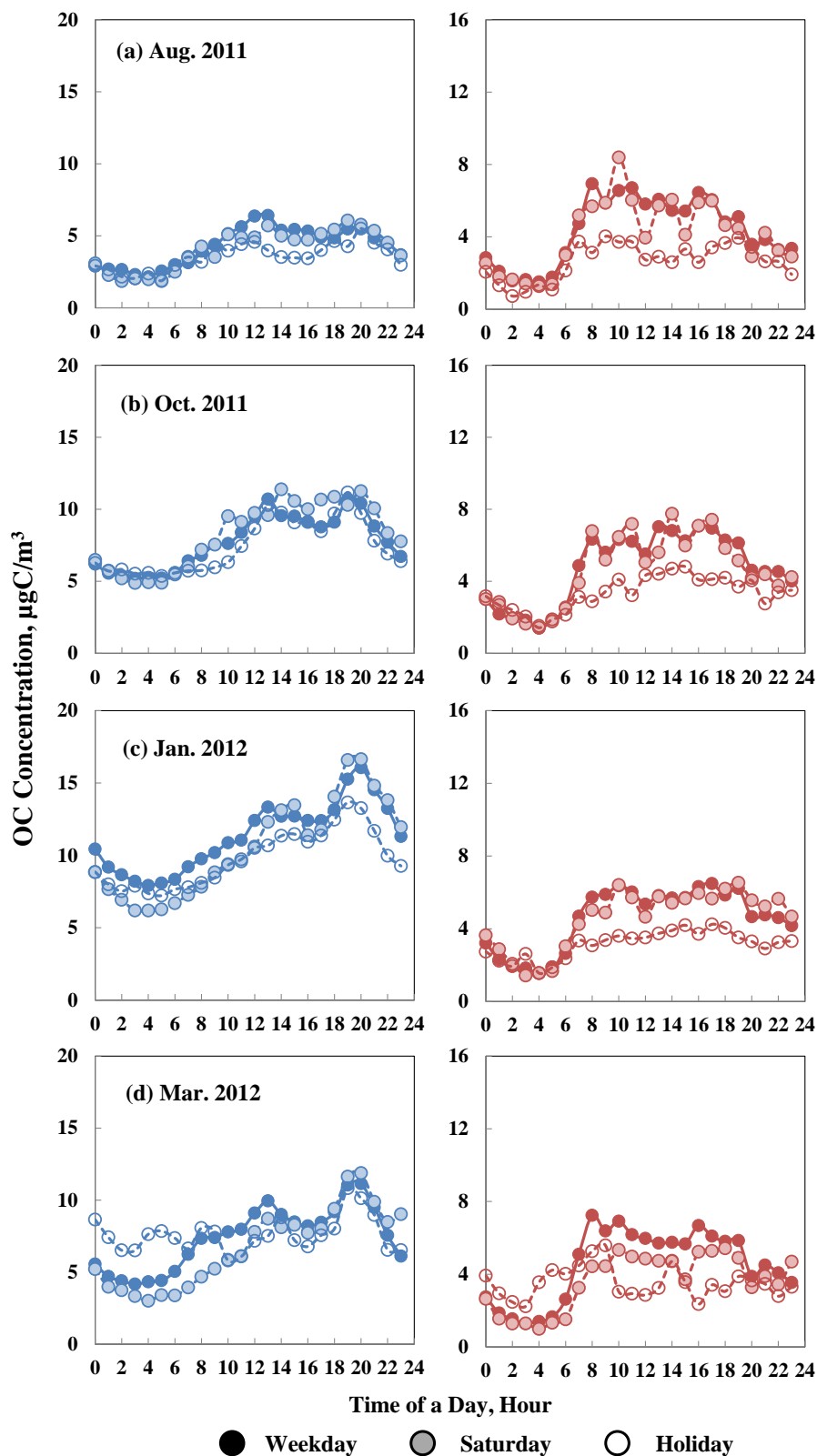


Figure 3. Diurnal variations of OC (blue dots) and EC (red dots) concentrations (unit: $\mu\text{gC}/\text{m}^3$) for weekdays, Saturdays and holidays at MK AQMS in (a) August 2011, (b) October 2011, (c) January 2012 and (d) March 2012.

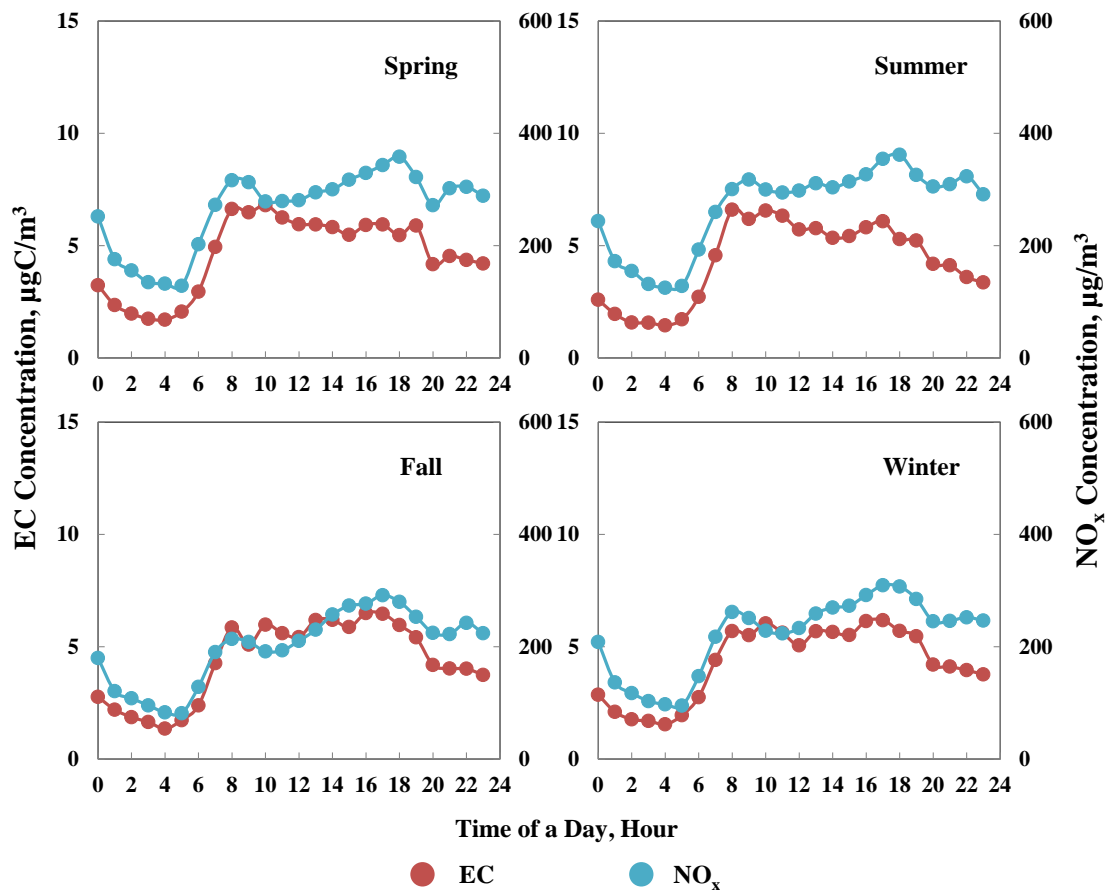


Figure 4. Diurnal variations of EC ($\mu\text{gC}/\text{m}^3$) and NO_x ($\mu\text{g}/\text{m}^3$) at MK AQMS during different seasons.

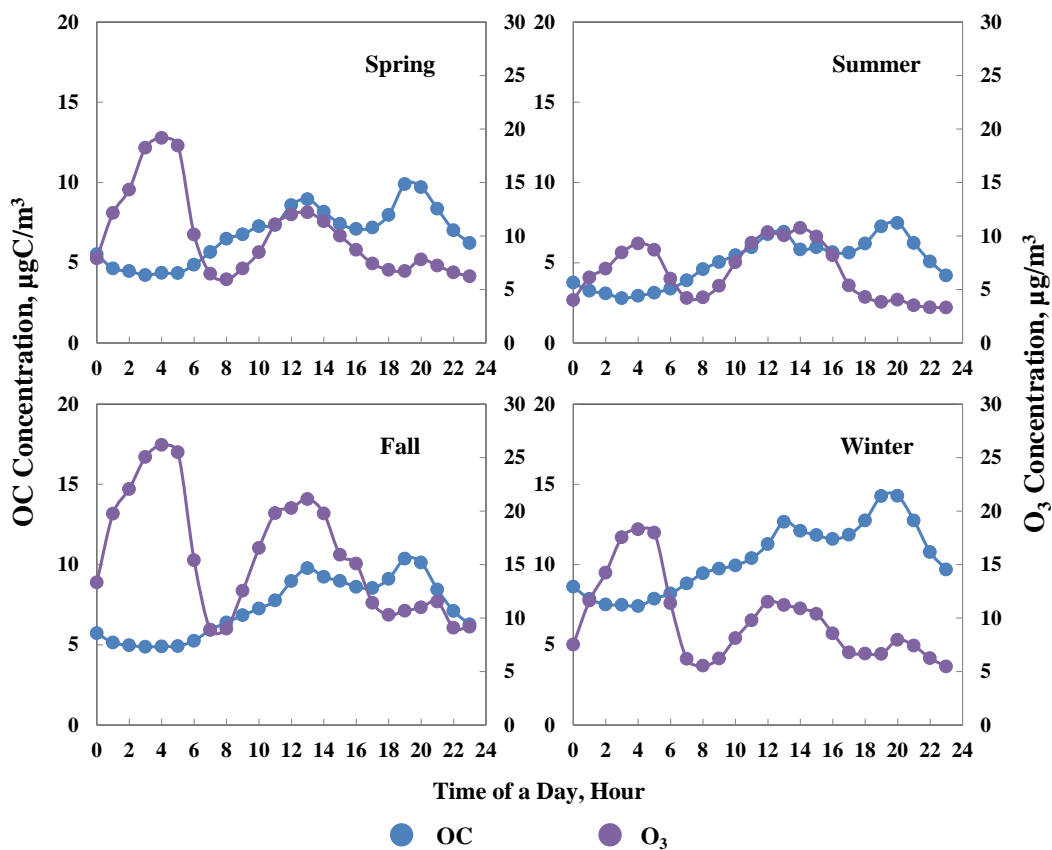


Figure 5. Diurnal variations of OC ($\mu\text{gC}/\text{m}^3$) and O_3 ($\mu\text{g}/\text{m}^3$) at MK AQMS during different seasons.

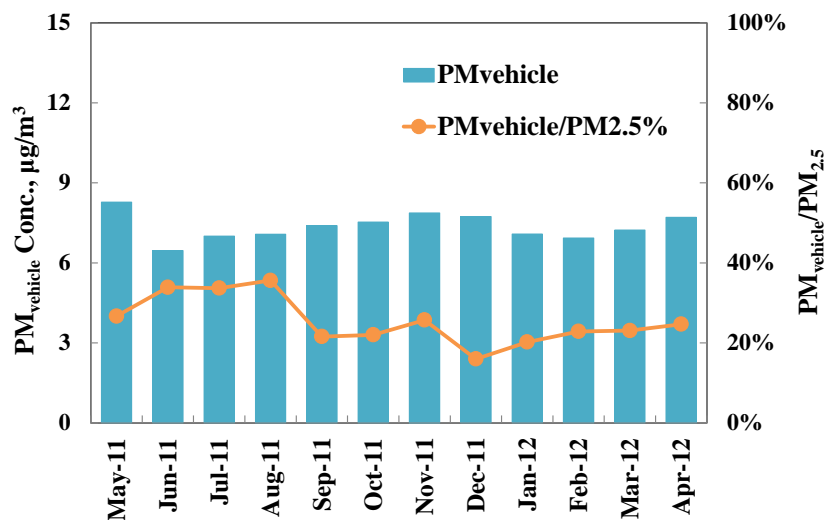


Figure 6. Monthly average vehicle-related $\text{PM}_{2.5}$ concentrations estimated by ($\text{OM}_{\text{vehicle}} + \text{EC}$) and the relative contributions to the monthly average $\text{PM}_{2.5}$ mass at MK AQMS during May 2011–April 2012. (Note: $\text{PM}_{2.5}$ mass concentrations were measured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

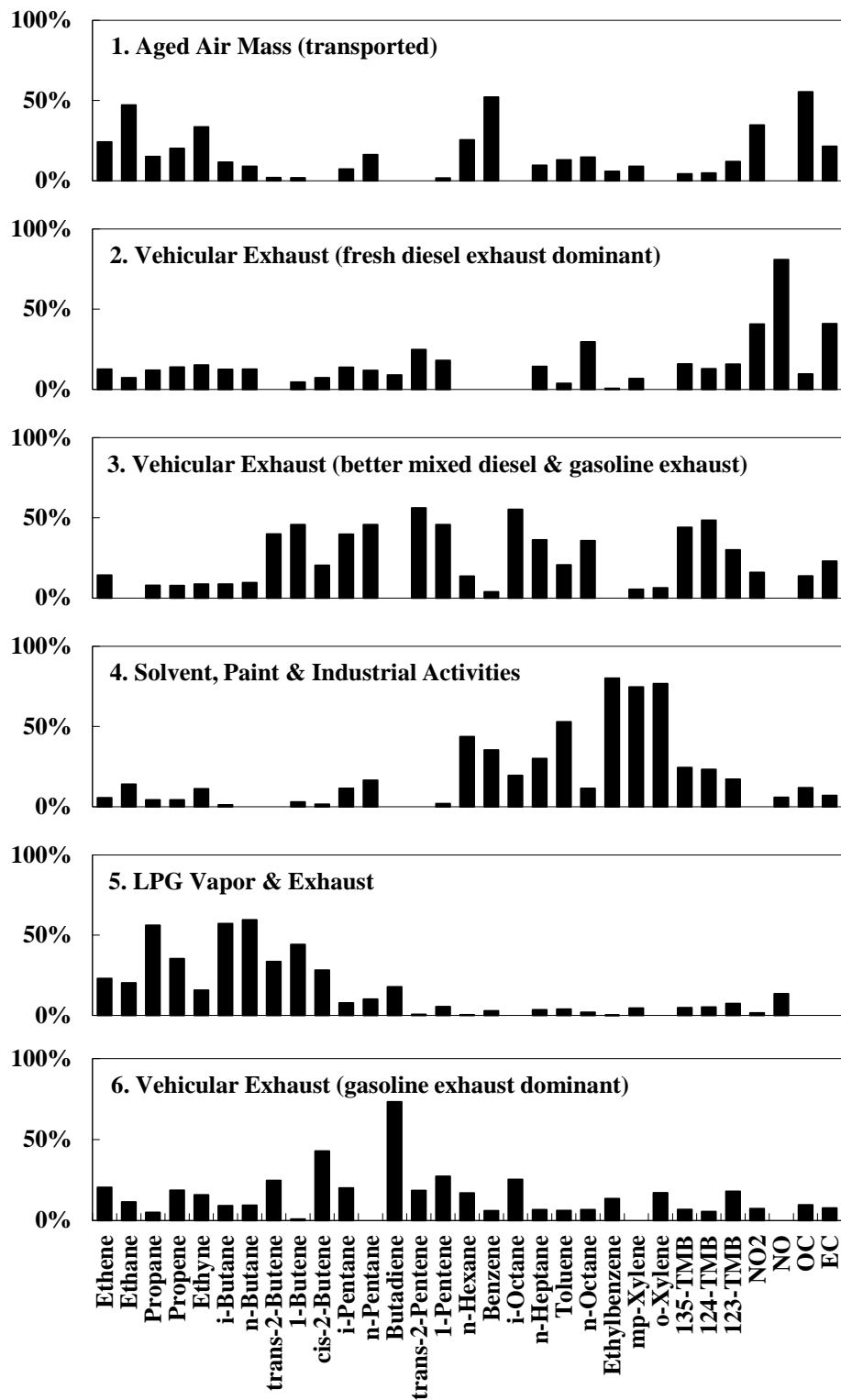


Figure 7. Source profile (% of species total) identified by USEPA PMF3.0.

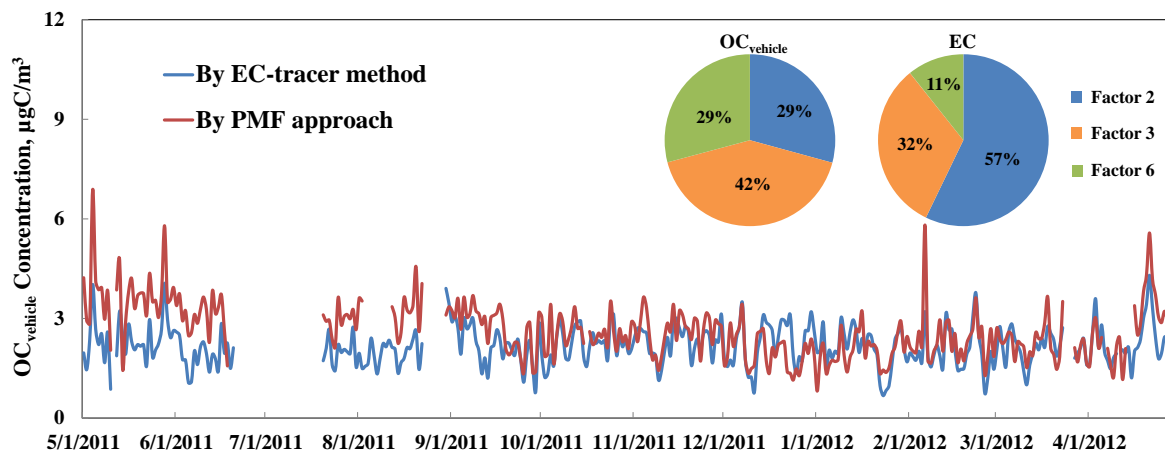


Figure 8. Time-series daily-averaged OC_{vehicle} (µgC/m³) estimated by EC-tracer method (blue curve) and by PMF approach (red curve) at MK AQMS during May 2011–April 2012. The relative contributions of different vehicular emission-related factors to the OC_{vehicle} and EC, estimated by PMF, are shown in the pie charts.