Carbonaceous Components in PM$_{2.5}$ and PM$_{0.1}$ with Online Measurements of Gaseous and Particulate Pollutants: Implication of Thermal-Optical Derived EC$_2$ Fraction as a Component of Ultrafine Particles in the Roadside Environment

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ABSTRACT

An investigation of the carbonaceous components of PM$_{2.5}$ ($D_p < 2.5$ µm) and PM$_{0.1}$ ($D_p < 0.1$ µm) in conjunction with online measurements of gaseous and particulate pollutants, which are dominated by motor vehicle emissions, was undertaken over 15 consecutive days in a field sampling campaign at a roadside and reference site for daytime (06:00 to 17:30) and nighttime (18:00 to 05:30) conditions. The results indicated that traffic-related air pollutants strongly influenced pollution levels in the sampling area, especially during the nighttime, although the concentrations were lower than during the daytime. Water-soluble organic carbon/organic carbon (WSOC/OC) ratios in PM$_{0.1}$ were 0.60 ± 0.11 and 0.63 ± 0.16 at the roadside and reference sites, respectively, while the corresponding ratios in PM$_{2.5}$ were found to be 0.60 ± 0.11 and 0.63 ± 0.14. These results demonstrated the relatively high contribution of WSOC in the study area compared to previous reports. It was observed that elemental carbon (EC) in PM$_{0.1}$ are emitted approximately by a factor of 0.1 in comparison with those observed for EC in PM$_{2.5}$ when considering the slopes of the linear relationship with particle-bound PAHs and NOx, while OC displayed no such relationship. Our measurements indicate that a significant portion of the OC in PM$_{0.1}$ is not directly co-emitted with EC from motor vehicles but is readily adsorbed or condensed onto the existing EC fractions through condensation. The relationship between the EC$_2$ fraction and the particle number concentration indicates that the EC$_2$ fraction is the primary chemical component of traffic related ultrafine particles in terms of particle number concentration.

Keywords: Carbonaceous components; Ultrafine particle; Fine particles; Roadside; EC$_2$ fraction.

INTRODUCTION

Carbonaceous aerosol can be classified as organic carbon (OC) and elemental carbon (EC). Methods for the determination of OC and EC have been introduced and developed (Novakov, 1981; Birch and Cary, 1996; Chow et al., 1993; Hitzenberger et al., 1996; Lavanchy et al., 1999; Chow et al., 2001; Fung et al., 2002). To determine carbonaceous components in PM$_{2.5}$ ($D_p < 2.5$ µm), several studies have used the thermal-optical reflectance (TOR) method based on the IMPROVE protocol (Chow et al., 1993; Cabada et al., 2002; Cao et al., 2003; Kim et al., 2003; Cabada et al., 2004; Cao et al., 2004; Chow et al., 2004; Kim et al., 2004; Han et al., 2007, 2009) while few studies have been undertaken to determine the carbonaceous components of PM$_{0.1}$ ($D_p < 0.1$ µm) (Sardar et al., 2005; Chen et al., 2010a, b; Zhu et al., 2010; Kim et al., 2011a, b; Kudo et al., 2011; Kudo et al., 2012; Zhu et al., 2012; Kim et al., 2013).

Carbonaceous aerosol is an important constituent of PM$_{2.5}$ in most of the U.S. Between 10–65% of the fine particulate mass in various regions of the country has been identified as carbonaceous material (Gray et al., 1986; Turpin and Huntzicker, 1991; Tolocka et al., 2001; Lim and Turpin, 2002; Seinfeld and Pandis, 2006). For PM$_{0.1}$ in Los Angeles, OC accounted for 32–69% and EC accounted for 1–34% of the chemical composition (Sardar et al., 2005). Another study in Japan also revealed that carbonaceous components accounted for 51–57% and 83–92% of the measured...
components (carbonaceous and ionic components) in PM$_{2.5}$ and PM$_{0.1}$ in the roadside environment over a 1-year sampling period, indicating that carbonaceous components are an important constituent of PM$_{2.5}$ as well as PM$_{0.1}$ (Kim et al., 2011a). Furthermore, Chen et al. (2010) reported that in roadside, tunnel, and forest sampling sites, 55, 59, and 43%, respectively, of the mass of PM$_{0.1}$ were carbonaceous components (Chen et al., 2010a). Although the sampling location, year, and equipment differ between these studies, all generally indicate that carbonaceous components are the main constituent of PM$_{0.1}$.

OC can be emitted directly from primary sources or formed via gas-to-particle conversion processes in the atmosphere (Jones and Harrison, 2005; Saylor et al., 2006). EC is a good tracer for fossil fuel combustion, including motor vehicle emissions. Biomass burning also emits EC at much lower levels and is an important source in winter conditions in rural or residential areas or during wildfire events (Gelencsér et al., 2007). WSOC also can also be used as an indicator of SOA formation because SOA compounds are water soluble and contain polar functional groups (such as hydroxyl, carbonyl, and carboxyl groups) as a result of atmospheric oxidation (Saxena and Hildemann, 1996), although some WSOC can also be produced by primary emissions such as biomass burning (Mayol-Bracero et al., 2002).

Primary ratios of OC to EC vary from source to source and display temporal and diurnal variations (Cabada et al., 2002; Cabada et al., 2004), but because EC is emitted only by combustion sources, gaseous tracers of combustion (CO, NO, and NO$_x$) can be used to determine periods dominated by primary aerosol emissions. Eight carbon fractions have been defined (OC1 – OC4, POC (pyrolyzed OC) and EC1 – EC3) by the IMPROVE protocol using the TOR method. Among the EC fractions, it has been reported for daytime and nighttime conditions. Third, the relationship of the EC2 fraction in PM$_{0.1}$ with particle number concentrations was investigated in comparison with data measured at the roadside in Saitama, Japan, where a similar atmospheric sampling campaign was undertaken under similar environmental conditions (i.e., sampling locations).

**EXPERIMENTAL**

**Sample Collection and Monitoring**

Sampling was undertaken for 15 consecutive days at the Korea Institute of Science and Technology (KIST), Seoul from 20 November to 4 December 2012. Field sampling was undertaken at a roadside and a reference site, which were about 50 and 240 m, respectively, distant from major roadways (Fig. 1). The samplers were 3 and 25 m above ground level (AGL) for the roadside and reference sites, respectively, with samplers placed on the roof of a mobile laboratory (ML) at the roadside site and on the roof of a three-story building on a hill at the reference site. The major roadways consisted of a four-lane overpass and an eight-lane underpass. The reference site was not defined as an urban background site but was a location where traffic emissions and urban background levels could be observed.

Traffic volume on the eight-lane underpass was measured throughout the measurement periods by an automatic vehicle detection system operated by the Seoul Metropolitan Police Agency Comprehensive Traffic Information Center. The daily average traffic volume of the eight-lane underpass ranged from 362 to 2,890 vehicles h$^{-1}$. The daytime (06:00 to 18:00) average traffic volume was ~23,000 vehicles (1,949 ± 253 vehicles h$^{-1}$), whereas the nighttime (18:00 to 06:00) average traffic volume was ~16,000 vehicles (1,360 ± 599 vehicles h$^{-1}$), indicating almost 1.5-fold more traffic during the daytime. According to Statistics Korea (2011), ~18.4 million motor vehicles are registered in the country, with vehicles powered by gasoline, diesel, and liquefied petroleum gas (LPG) accounting for 49.7, 36.4, and 13.2% of the total, respectively. Of the total number of motor vehicles in Korea, 16.2% are registered in Seoul.

A roadside and a reference sampling site were selected to determine the influence of roadways. By the time of the winter monsoon (i.e., during the sampling periods) wind generally blows from northwest to southeast; thus we expected that the underpass roadway would mainly influence the roadside sampling site directly, while the reference site would be influenced indirectly by both the underpass and the overpass. The two sites were located downwind of the roadways so that the impact of motor vehicles could be observed. PM$_{2.5}$ and PM$_{0.1}$ in conjunction with online measurements of gaseous and particulate pollutants, which are dominated by motor vehicle emissions. First, the diurnal variation of gaseous and particulate pollutants using an online instrument was assessed, together with traffic volumes. Second, carbonaceous components in PM$_{2.5}$ and PM$_{0.1}$ were reported for daytime and nighttime conditions. Third, the relationship of the EC2 fraction in PM$_{0.1}$ with particle number concentrations was investigated in comparison with data measured at the roadside in Saitama, Japan, where a similar atmospheric sampling campaign was undertaken under similar environmental conditions (i.e., sampling locations).
**Meteorological Data and Other Pollutants**

An ML equipped with various real-time instruments for gaseous and particulate pollutants was used to measure air pollutant concentrations at the roadside site. A fast mobility particle sizer (FMPS Model 3091, TSI Inc., Shoreview, MN, USA) was used to measure the particle number size distribution with the particle mobility diameter $D_p$ at a flow rate of 10 L min$^{-1}$ at the roadside site. The electrometer backgrounds were monitored and set to zero using particle-free air before each measurement. In the present study, UFPs size range was defined from 6 to 560 nm in mobility diameter. An aethalometer (AE42 seven-wavelength, Magee Scientific, Berkeley, CA, USA) and nanoparticle aerosol monitor (NAM Aerotrak 9000, TSI Inc. St. Paul, MN, USA) were installed at the reference site for the measurement of black carbon (BC) and the lung-deposited surface area (LDSA: Alveolar region;
to estimate the difference in BC and particle surface area between the two sampling sites. Detailed information from the real-time instruments at the roadside and reference sites is shown in Table 1. Meteorological data was acquired from the nearest automatic weather station (AWS) at Seongbuk-gu, which was located 3 km from the sampling sites.

The prevailing wind (i.e., 40% of the total measurement days) blew from the west–northwest (WNW) with a moderate wind speed (1.4 ± 1.0 m s⁻¹) during the daytime while the wind blew from the northwest (NW) for 65% of the nighttime measurement period with a moderate wind speed (1.6 ± 1.2 m s⁻¹). The wind data indicate that our sampling sites were directly influenced by the emissions from motor vehicles, especially during the nighttime. Although the prevailing wind direction during the daytime was WNW, the wind blew from various directions, indicating that air pollution levels during the daytime were influenced not only by the roadways but also other sources, such as surrounding forest or residential areas.

**Analysis of Carbonaceous Components**

Carbonaceous components were analyzed using a Desert Research Institute (DRI) Model 2001 Carbon Analyzer (Atmoslytic Inc., Calabasas, CA) following the IMPROVE_TOR method. Inside of the analyzer during the analysis, the sample was heated to produce four OC fractions (OC1, OC2, OC3, and OC4) at temperatures of 120, 250, 450, and 550°C, respectively, in a non-oxidizing helium atmosphere, as well as three EC fractions (EC1, EC2, and EC3) at 550, 700, and 800 °C, respectively, in an oxidizing atmosphere of 2% O₂/98% He. At the same time, pyrolyzed OC (POC) is produced in the inert atmosphere, which decreases the reflected light to correct for charred OC (Chow et al., 1993; Kim et al., 2011a, b).

One quarter of each filter was placed in 5 mL of distilled water in a 20-mL amber-glass vial, which was then sealed with a cap and Teflon tape to prevent volatilization of organic compounds, and placed in an ultrasonic bath for 60 min for sample extraction. The temperature of the ultrasonic bath was maintained below 10°C using ice packs. The extraction efficiency exceeded 95%, and the field blanks were also analyzed. After the extraction, the water-soluble organic compound (WSOC) content was determined on a total organic compound analyzer (TOC-V, Shimadzu, Japan). Water-insoluble organic compound (WIOC) content was defined as the total OC minus the WSOC content.

PM sampling with quartz filters may lead to either positive artifacts due to the adsorption of gas-phase OC or negative artifacts by the volatilization of OC (Kim et al., 2013). Recently, positive OC artifacts of PM$_{2.5}$ and PM$_{0.1}$ were estimated for forest, roadside, and highway tunnel samples using the quartz behind quartz (QBQ) method (Chen et al., 2010a, b; Zhu et al., 2010, 2012). These studies reported that the positive OC artifacts accounted for 51.6 and 20% at the roadside and tunnel locations, respectively, for UFPs ($D_p < 0.18$ µm); and 7.5 and 12.9% at the roadside and tunnel, locations, respectively, for FPs (0.18 < $D_p$ < 2.5 µm) (Chen et al., 2010a, b). However, complicated factors such as sampling
mechanism of equipment, flow rate, deposit area for sampling, saturation of adsorbed gases and evaporation rates of semi-volatile organic compounds, particle size, temperature, relative humidity, particle composition, and source characteristics (diesel, gasoline, and wood smoke) can influence on these artifacts. Furthermore, there is no simple way to correct for sampling artifacts using current measurements (Chow et al., 2010). For these reasons, unfortunately, we did not consider the correction of OC artifacts in our measurement because there is no simple way to correct for sampling artifacts using current measurements although QBQ method has been widely used for correction of only positive artifact. Further study has to be investigated and addressed the possible OC artifacts.

RESULTS AND DISCUSSION

**Diurnal Variations of Gaseous and Particulate Pollutants and the Relationship with Traffic Volume**

Table 2 shows the average temperature, relative humidity, and pollutant concentrations at the roadside site. Concentrations of gaseous and particulate pollutants were higher in the daytime than at nighttime. However, the concentrations were relatively high during the nighttime when the reduced traffic volume is considered, possibly due to the inhibition of pollutant mixing as a consequence of the stable atmospheric conditions.

The diurnal variations of traffic volume, gaseous (CO$_2$ and NO$_x$), and particulate (BC, particle-bound PAHs, and LDSA) pollutants, and the relationship of traffic volume with particle-bound PAHs, and NO$_x$ during the measurement periods at the roadside site are shown in Figs. 2(a), 2(b), and 2(c), respectively. The diurnal variation of gaseous and particulate pollutants exhibits two peak pollutant concentrations during the morning and evening rush hours. The traffic volume increased from 5:00 and peaked at 8:00, with a high volume of traffic continuing until 18:00. The traffic volume then decreased gradually until 4:00. These observations indicate that the roadways had more influence during the nighttime than the daytime when the prevailing wind direction is taken into consideration (Fig. 3). LDSA at both sites also displayed a similar tendency with a strong correlation (daytime: $y = 0.85x - 3.84$, $r^2 = 0.72$; nighttime: $y = 1.01x - 7.15$, $r^2 = 0.83$; $x$-axis = roadside, $y$-axis = reference) (Supplementary Fig. S1). The higher correlation coefficient for nighttime conditions indicates that the roadways had more influence during the nighttime than the daytime when the prevailing wind direction is taken into consideration. Linear regressions of BC observed at the roadside and reference sites produced strong correlations with slopes of 0.64 ($r^2 = 0.76$) and 0.75 ($r^2 = 0.84$) for daytime and nighttime conditions, respectively, ($x$-axis = BC at roadside, $y$-axis = BC at reference) (Supplementary Fig. S1).

BC concentrations at the roadside site were 5.2 ± 3.2 and 4.4 ± 3.0 µg m$^{-3}$ for daytime and nighttime, respectively, while BC concentrations at the reference site were 3.4 ± 2.4 and 3.2 ± 2.5 µg m$^{-3}$ for daytime and nighttime, respectively. Approximately 1.5-fold more BC was observed at the roadside than the reference site, indicating the direct influence of motor vehicle emissions at the roadside. In contrast, LDSA concentrations at the roadside were 55.3 ± 21.5 and 49.3 ± 20.2 µm$^2$ cm$^{-3}$ for daytime and nighttime, respectively, while those at the reference site were 40.0 ± 19.4 and 38.7 ± 18.6 µm$^2$ cm$^{-3}$ for daytime and nighttime, respectively. The two rush hour peaks for BC and LDSA at both sites suggest that motor vehicle emissions are the main source of BC and submicron particles (D$_p$ < 1 µm) in the study area.

**Carbonaceous Components of PM$_{2.5}$ and PM$_{1.0}$**

OC accounted for 73 and 79% of the total carbon (TC) in PM$_{2.5}$ in the combined 23-h samples at the roadside and reference sites, respectively, while OC accounted for 82 and 88% of the TC in PM$_{1.0}$ for the combined 23-h samples at the roadside and reference sites, respectively. The

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**Table 2.** Average concentrations of gaseous and particulate pollutants in the daytime and nighttime at the roadside site.

<table>
<thead>
<tr>
<th>Meteorological factors and air pollutant concentrations</th>
<th>Daytime</th>
<th>Nighttime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>4.0 ± 2.0</td>
<td>1.5 ± 2.5</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>52.0 ± 10.9</td>
<td>60.2 ± 9.6</td>
</tr>
<tr>
<td>Particle number concentration (particles cm$^{-3}$)</td>
<td>2.6 ± 0.4× 10$^4$</td>
<td>2.1 ± 0.6× 10$^4$</td>
</tr>
<tr>
<td>BC concentration (µg m$^{-3}$)</td>
<td>5.2 ± 3.2</td>
<td>4.4 ± 3.0</td>
</tr>
<tr>
<td>Particle-bound PAHs concentration (ng m$^{-3}$)</td>
<td>45.7 ± 19.0</td>
<td>34.2 ± 19.6</td>
</tr>
<tr>
<td>Surface area concentration (µm$^2$ cm$^{-3}$)</td>
<td>55.3 ± 21.5</td>
<td>49.3 ± 20.2</td>
</tr>
<tr>
<td>CO$_2$ concentration (ppm)</td>
<td>491.3 ± 32.5</td>
<td>491.5 ± 33.5</td>
</tr>
<tr>
<td>CO concentration (ppm)</td>
<td>1.0 ± 0.5</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td>NO$_x$ concentration (ppb)</td>
<td>147.5 ± 69.0</td>
<td>127.3 ± 82.5</td>
</tr>
</tbody>
</table>
Fig. 2. Diurnal variation of traffic volume, gaseous (CO₂ and NOₓ), and particulate (BC, particle-bound PAHs, and LDSA) pollutants during the measurement periods at the roadside site (a) and the relationship of traffic volume with particle-bound PAHs (b) and NOₓ (c) measured at the roadside site.

Fig. 3. Wind speed and direction in the daytime (a) and nighttime (b) during the measurement periods.
carbonaceous components at the roadside and reference sites for daytime and nighttime are shown in Fig. 4 as average concentrations (with standard deviations). Minor differences displayed in Figs. 4(a) and 4(b) are within the standard deviations for WSOC and WIOC between the roadside and reference sites in PM$_{2.5}$ and PM$_{0.1}$. EC fraction concentrations were higher in roadside samples than in the reference site samples, indicating the influence of motor vehicle emissions at the roadside sampling area. OC fraction concentrations in samples at the two sites were similar, which suggested contributions of other sources, such as air mass transport, biomass burning, and secondary organic aerosol (SOA). Similarly, only minor differences in the OC concentrations between daytime and nighttime samples were observed, whereas EC concentrations in the nighttime samples were slightly higher than in the daytime samples.

Although some WSOC can be produced by primary emissions such as biomass burning, they can be used as an indicator of SOA formation because SOA compounds are water soluble and contain polar functional groups as a result of atmospheric oxidation. In our study area, the WSOC/OC ratios in PM$_{0.1}$ were 0.60 ± 0.11 and 0.63 ± 0.16 at the roadside and reference sites, respectively. The ratios in PM$_{2.5}$ were similar, 0.60 ± 0.11 and 0.63 ± 0.14 at the roadside and reference sites, respectively. Insignificant differences for WSOC and WIOC between the roadside and reference sites for both PM$_{2.5}$ and PM$_{0.1}$. These WSOC/OC ratios are higher than those reported for the roadside environment in Japan (0.54 for fall and 0.42 for winter in PM$_{2.5}$) (Kim et al., 2011a), indicating that WSOC make a considerable contribution in our study area. This contribution of WSOC may have been due to the formation of SOA or biomass burning.

The OC/EC ratio as a function of EC is shown in Fig. 5 for PM$_{2.5}$ (a) and PM$_{0.1}$ (b) at the roadside and reference sites. The OC/EC ratios presented in this study were obtained without OC corrections for both positive and negative artifacts thus these ratios cannot be directly compared with studies considered OC correction for the artifacts. OC/EC ratios in PM$_{2.5}$ ranged from 2.0–3.9 and 2.5–6.4 for the roadside and reference sites, respectively, with ratios being higher at the reference site than the roadside site. Daytime and nighttime OC/EC ratios for PM$_{2.5}$ displayed a similar pattern, with a higher ratio in the nighttime (roadside: 3.2 ± 0.5; reference: 4.2 ± 1.1) than daytime (roadside: 2.6 ± 0.5; reference: 3.6 ± 0.9) samples. The higher OC/EC ratios at the reference site with a diurnal pattern that had higher ratios during nighttime, reflects the influence of motor vehicle emissions at both sites during daytime.

Relatively high OC/EC ratios were observed for PM$_{0.1}$ samples (Fig. 5(b)). The OC/EC ratios in PM$_{0.1}$ were 2.6–11.3 and 5.1–50.0 for roadside and reference sites, respectively. The higher and lower ratios at the reference and roadside sites, respectively, are consistent with the result for PM$_{2.5}$. Unlike the results for PM$_{2.5}$, the OC/EC ratios in PM$_{0.1}$ displayed a diurnal pattern only at the roadside site (daytime: 5.3 ± 2.3; nighttime: 6.6 ± 2.0), possibly due to the low EC concentrations in PM$_{0.1}$ at the reference site.

Relationship of OC and EC in PM$_{2.5}$ and PM$_{0.1}$ with Online Measurement Data

To clarify the influence of motor vehicle emissions on the carbonaceous components in PM$_{2.5}$ and PM$_{0.1}$ in the study area, the relationships of OC and EC were plotted using real-time measurement data. Fig. 6 shows the relationships of OC and EC with particle-bound PAHs and NO$_x$ in PM$_{2.5}$ and PM$_{0.1}$ at the roadside site. Large percentage of energy consumption with coal combustion can lead to significant

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**Fig. 4.** Observed WSOC, WIOC, and EC concentrations in PM$_{2.5}$ and PM$_{0.1}$ at the roadside and reference sites (Error bars indicate the standard deviations of measured concentrations ($n$ = 15)).
emissions of particle-bound PAHs and NOx influencing in our obtained result. Thus, the energy consumption of coal combustion in Seoul should be provided. According to the Seoul Metropolitan Government (2013), coal consumption accounts for only 0.8% of the total energy consumption in Seoul. Thus, we strongly believe that the contribution of coal combustion sources would be minimal, especially, when we consider the sampling locations. Both particle-bound PAHs and NOx are emitted primarily from motor vehicles, especially diesel vehicles (Nielsen, 1996; Kozawa et al., 2009; Levy et al., 2001, 2003; Kim et al., 2014). As shown in Fig. 6, the OC and EC fractions in PM$_{2.5}$ and PM$_{0.1}$ exhibited strong relationships with particle-bound PAHs and NOx, indicating the considerable contribution of motor vehicle emissions in the study area. As mentioned previously, EC is a good tracer of fossil fuel combustion; i.e., motor vehicle emissions from road transport in urban areas. In contrast, OC can be formed by secondary production in the atmosphere as well as direct emission from motor vehicles. The weaker relationship of OC with particle-bound PAHs and NOx suggests that some OC was not primary but originated from other sources. For PM$_{0.1}$, EC also displayed a strong relationship with particle-bound PAHs and NOx. From the slopes of the linear regression analysis, it can be concluded that EC in PM$_{0.1}$ are emitted approximately by a factor of 0.1 in comparison with those observed for EC in PM$_{2.5}$. The OC in PM$_{0.1}$ had weaker relationships with particle-bound PAHs and NOx than the OC in PM$_{2.5}$. This suggests that a significant portion of the OC in PM$_{0.1}$ was not directly co-emitted with the EC from motor vehicles but was readily adsorbed or condensed onto the existing EC fractions through condensation.

**The EC2 Fraction as the Main Component of Ultrafine Particles**

Strong relationships between the particle number concentrations (5.6 < $D_a$ < 560 nm) and BC ($r^2 = 0.34, n = 30$), particle-bound PAHs ($r^2 = 0.62, n = 30$), and NOx ($r^2 = 0.56, n = 30$) were observed during our measurements, indicating that particle number concentrations were closely related to motor vehicle emissions in the study area. To determine the relationship of particle number concentration with the measured carbon fractions over the 15-day measurement period, both were plotted.

Among the carbon fractions, only EC2, which can be generated at > 700°C in an oxidizing atmosphere of 2% O$_2$-98% He following the IMPROVE protocol with the TOR method, displayed a strong relationship with the particle number concentration. To confirm this observation, we plotted the same linear relationship for measurements at the roadside of Saitama, Japan 2011 as shown in Table 3 (Kim et al., 2013). Fig. 6 shows the EC2 fraction in PM$_{2.5}$. The EC2 fraction in PM$_{2.5}$ had a moderate relationship with the particle number concentration, indicating that the EC2 fraction in PM$_{0.1}$ was more closely related to the particle number concentration.

It has been reported that the EC1 fraction, as analyzed by the IMPROVE protocol using the TOR method, can contain a large quantity of EC that originated from biomass burning, whereas the EC2 fraction contains mainly of diesel soot and has greater resistance to thermal oxidation and a more graphitic, rigid, and highly aromatic structure than the EC1 fraction (Han et al., 2007). Therefore, it can be concluded that the EC2 fraction in PM$_{0.1}$ in the study area was mainly emitted from motor vehicles.

The size distributions of EC particles from vehicular and biomass burning emissions also support our finding. Primary EC particles formed in internal combustion engines have geometric mean diameter (GMD) ranging from 10 to 50 nm spherules and they cluster together immediately after their formation in a flame to form aggregates, which are their most stable form (Wentzel et al., 2003). On the other hand, EC particles associated with the smoldering stage of biomass combustion usually are present as much larger spherical particles (Martins et al., 1998). Another study also reported from their study on BC that urban BC was consistently associated with smaller sizes than biomass burning BC (Schwarz et al., 2008).

Consequently, the relationship of the EC2 fraction with the particle number concentration reflects the fact that the
EC2 component is the primary chemical component of traffic related ultrafine particles in terms of particle number concentration. Although plotting the data points yielded a linear fit, a sigmoid curve would provide a better fit, possibly due to the coagulation and aggregation of ultrafine particles following the emission of a high number of small soot particles within a limited space (Supplementary Fig. S2).

**CONCLUSIONS**

Distinct diurnal variations in traffic volume, gaseous (CO₂ and NOₓ), and particulate (BC, particle-bound PAHs, and LDSA) pollutants were observed, together with a distinct relationship between traffic volume and air pollutants. Observations, which took into consideration the prevailing wind direction, indicated a considerable influence of traffic-related air pollutants on pollution levels in the sampling area, especially during the nighttime due to atmospheric stability, although the concentrations were lower than those during the daytime. Approximately 1.5-fold more BC was observed at the roadside than the reference, indicating the direct influence of motor vehicle emissions.

OC accounted for 73 and 79% of the total carbon (TC) in PM₂.₅ for the combined 23-h samples at the roadside and reference sites, respectively, while OC accounted for 82 and 88% of the total carbon (TC) in PM₀.₁ for the combined 23-h samples at the roadside and reference sites, respectively, indicating a significant contribution of OC in the study area. Relatively high WSOC/OC ratios in PM₂.₅ and PM₀.₁ at the roadside and reference sites indicate a considerable

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**Table 3.** Linear regressions of the EC₂ fraction (x-axis) with mean particle number concentration (y-axis) at roadside sites in Seoul, Korea and Saitama, Japan.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Measurement period</th>
<th>Slope</th>
<th>y-Intercept</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seoul, Korea (This study)</td>
<td>Nov.–Dec. 2012</td>
<td>5.6 × 10⁷</td>
<td>1.4 × 10⁷</td>
<td>0.48</td>
</tr>
<tr>
<td>Saitama, Japan (Kim et al., 2013)</td>
<td>Jan. 2011</td>
<td>5.5 × 10⁷</td>
<td>2.0 × 10⁷</td>
<td>0.60</td>
</tr>
<tr>
<td>Seoul + Saitama</td>
<td></td>
<td>1.0 × 10⁸</td>
<td>2.3 × 10⁴</td>
<td>0.61</td>
</tr>
</tbody>
</table>
contribution of WSOC in the study area, possibly due to SOA formation or biomass burning. OC/EC ratios in PM$_{0.1}$ ranged from 2.6–11.3 and 5.1–50.0 for the roadside and reference sites, respectively, with higher ratios at the reference site.

For PM$_{2.5}$ and PM$_{0.1}$, EC displayed a strong relationship with particle-bound PAHs and NO$_x$, indicating that EC in PM$_{0.1}$ is emitted approximately by a factor of 0.1 in comparison with those observed for EC in PM$_{2.5}$, based on the slope of the linear relationship. Unlike the relationship between OC in PM$_{2.5}$ and particle-bound PAHs and NO$_x$, the relationships of OC with these pollutants in PM$_{0.1}$ were weak. This suggests that a significant portion of the OC in PM$_{0.1}$ is not directly co-emitted with EC from motor vehicles but is readily adsorbed or condensed onto the existing EC fractions through condensation.

The relationship between the EC2 fraction and particle number concentrations indicates that EC2 is the primary chemical component of traffic related ultrafine particles in terms of particle number concentration. Although plotting the data points yielded a linear fit, a sigmoid curve would provide a better fit, possibly due to the coagulation and aggregation of ultrafines particles following the emission of a high number of small soot particles within a limited space. However, the EC2 differences between the traffic and the reference site and its direct dependence on traffic volume may help to prove EC2 origin in motor emissions.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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