Concentration Variations in Primary and Secondary Particulate Matter near a Major Road in Korea

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ABSTRACT

Particle-phase concentrations were measured at 10, 80, and 200 m from the roadside of a national highway near Seoul in January and May 2008. The highway has two lanes each way, with an average hourly traffic volume of 1,070 vehicles. In January 2008, PM10 concentrations decreased from 10 to 80 m but increased at 200 m. Black carbon (BC) decreased only slightly with distance due to the influence of biomass burning and open burning from the surrounding areas. In May 2008, the effect of secondary formation on both PM10 and PM2.5 was significant due to high temperatures compared with January. Because on-road emissions had little effect on secondary formation for a short time, variations in PM10 concentrations became smaller, and PM2.5 concentrations increased with distance. The effects of fugitive dust on PM concentrations were greater in May than in January when the mean temperature was below freezing. In the composition variations, the amounts of primary ions, organic carbon (OC), and BC were larger in January, while those of secondary ions and others were larger in PM10, as well as PM2.5 in May.

Key words: Vehicle emissions, Biomass burning, Open burning, Fugitive dust, Secondary formation

1. INTRODUCTION

Roadside pollution is of particular concern because cars account for a significant part of urban life (US EPA, 2000). Primary attention has been given to the risk of vehicle emissions in roadside pollution (WHO, 2010; US EPA, 2002), the key air pollutants of which are soot and ultrafine particles. Hitchins et al. (2000) argued that: (1) construction of buildings in areas directly affected by the roads should be avoided; (2) appropriate filtration systems should be installed if a building is constructed in such areas; and (3) buildings such as schools, in which the filtration system is not fully effective, should be set back a considerable distance from roads.

It is generally understood that vehicle emissions from major roads mostly affect areas up to about 200 to 300 m from the roadside. Carbon monoxide (CO), black carbon (BC), and the number concentration of particles, most of which come from vehicle exhaust, clearly decrease with distance from the roadside (Zhu et al., 2002a, b). In contrast, variations in particulate matter (PM; PM10 [particles with an aerodynamic diameter of 10 μm or less] and PM2.5 [particles with an aerodynamic diameter of 2.5 μm or less]) with distance are indistinct because PM has a variety of emission sources other than vehicle emissions (Zhu et al., 2002a; Roorda-Knape et al., 1998).

In Korea, air pollutants, including volatile organic compounds (VOCs), BC, and ultrafine particles, have been measured at road sides by several research groups (Ryoo et al., 2010; Woo et al., 2008; Lee et al., 2007). Woo et al. (2011) measured air pollutants in particle and gas phases from two-stroke scooters by driving mode. Yim et al. (2008) examined NO2 concentrations measured with a passive sampler at 40 locations along roadsides and at 6 locations in urban areas. Lee et al. (2011) compared concentrations of toxic VOCs measured at tunnels, and a roadside and residential area. They only measured concentrations of air pollutants at fixed locations of the roadside but did not examine the
variations in concentrations with distance.

In this study, PM$_{10}$, PM$_{2.5}$, and their ionic components as well as OC/BC in PM$_{10}$ were measured at the roadside of National Highway 45, which is located in front of the Global Campus of Hankuk University of Foreign Studies (HUFS). This approach is similar to that of Zhu et al. (2002a, b) and Roorda-Knape et al. (1998) in that concentrations of air pollutants were measured with distance from the roadside. They examined concentration variations with a focus on vehicle emissions. In contrast, this study investigated in what manner PM$_{10}$ and PM$_{2.5}$ at the roadside are associated with surrounding areas by differentiating primary and secondary pollutants based on major components of these pollutants.

2. METHODOLOGY

2.1 Measurement Site and Period

Particle-phase concentrations were measured at the roadside of National Highway 45, which is located about 35 km southeast of downtown Seoul and runs in front of the Global Campus of HUFS (see Fig. 1). This site was selected because: (1) there are no other thoroughfares except the access road to HUFS to the south; (2) there are no major emission sources except vehicle emissions from the roads; and (3) the surrounding areas have relatively flat terrain, where small-sized buildings, farmlands, and open spaces are scattered. In fact, fugitive dust from nearby farmlands or vacant lots also could become an important emission source. However, it was thought that its effect should be examined separately if fugitive dust is another key factor in determining particulate matter concentrations in Korea (Korean Society for Atmospheric Environment, 2009).

National Highway 45 around the measurement site has two lanes in each direction. Its average daily traffic volume of 1,070 vehicles is not as high as that for highways or thoroughfares of the city center, and it remains constant, except for a decrease in the middle of the night or weekend (Korea Ministry of Construction and Transportation, 2006). Passenger cars and light trucks on National Highway 45 account for the majority of the total traffic volume (about 95%), while buses and heavy trucks account for about 3.1% and 0.2%, respectively.

Measurements were carried out during two different periods - January 4 through 24, 2008, and May 11 through 29, 2008 (Table 1). The former period was chosen to represent the winter with high combustion-related emissions, while the latter was chosen for comparison with winter emissions. Three measurement locations were established at 10, 80, and 200 m from the northbound outer lane of the highway. The maximum distance of 200 m was chosen because it has been reported that direct influence of on-road emissions becomes insignificant beyond a distance of about 200 to 300 m (Zhu et al., 2002a, b; Roorda-Knape et al., 1998). Wind direction and speed were measured at a height of about

Fig. 1. Locations of the Global Campus Hankuk University of Foreign Studies (HUFS) in Korea, National Highway 45, and the measurement site. Low-volume air samplers were deployed at distances of 10, 80, and 200 m from the outer lane of two lanes each way.
was roughly 1.5 m above the surface. Samples for measuring OC and BC concentrations using a quartz filter were analyzed using a Metrosep A Supp 5 column with a standard deviation of 1.35 ± 0.29 µg/m³ each. The sampling height was conditioned at 40% relative humidity for 24 hours a.m., except in special circumstances. Teflon filters first soaked with ethanol in a vial to facilitate the contact with distilled water. After filling the vial with distilled water, ions were eluted using ultrasonic extractor (Power Sonic #420, Hwashin Tech). Detailed procedures for handling filters are described in Won et al. (2010) and Kim et al. (2015).

Three anions (Cl⁻, NO₃⁻, and SO₄²⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) were analyzed using a Metrohm’s module ion chromatography (IC). Anions were analyzed using a Metrosep A Supp 5 column with

### Table 1. Means and standard deviations of mass and components of PM₁₀ and PM₂.₅ with distance from the roadside during the measurement periods.

|       | January 4-24, 2008 | May 11-29, 2008 |
|-------|--------------------|-----------------|
|       | 10 m | 80 m | 200 m | 10 m | 80 m | 200 m |
| (a) PM₁₀ Number of data 16 10 |
| Mass  | 55.61 ± 27.55 43.96 ± 19.56 46.17 ± 22.24 | 61.46 ± 20.89 55.71 ± 20.76 59.48 ± 20.92 |
| OC    | 13.60 ± 6.80 12.33 ± 5.73 11.61 ± 5.67 | 10.42 ± 3.39 9.95 ± 3.26 8.73 ± 2.60 |
| BC    | 3.60 ± 1.35 3.22 ± 1.59 2.96 ± 1.18 | 3.46 ± 0.89 2.61 ± 0.79 2.34 ± 0.65 |
| Cl⁻   | 6.19 ± 3.58 4.61 ± 2.56 5.23 ± 2.85 | 0.81 ± 0.66 0.84 ± 0.63 0.65 ± 0.54 |
| NO₃⁻  | 11.19 ± 9.23 8.59 ± 5.77 10.10 ± 7.43 | 9.12 ± 4.12 8.58 ± 3.72 8.51 ± 3.30 |
| SO₄²⁻ | 6.30 ± 4.71 4.99 ± 2.64 5.65 ± 3.52 | 13.71 ± 7.50 13.17 ± 6.78 13.79 ± 6.82 |
| Na⁺   | 0.40 ± 0.21 0.50 ± 0.71 0.32 ± 0.10 | 0.19 ± 0.06 0.26 ± 0.09 0.62 ± 0.17 |
| NH₄⁺  | 6.52 ± 4.58 5.13 ± 2.96 5.88 ± 3.70 | 7.77 ± 3.64 7.17 ± 3.28 7.28 ± 3.27 |
| K⁺    | 1.00 ± 0.64 0.81 ± 0.43 0.91 ± 0.51 | 0.71 ± 0.34 0.80 ± 0.30 0.76 ± 0.31 |
| Mg²⁺  | 0.11 ± 0.05 0.09 ± 0.04 0.10 ± 0.04 | 0.05 ± 0.02 0.05 ± 0.03 0.05 ± 0.03 |
| Ca²⁺  | 0.64 ± 0.25 0.46 ± 0.17 0.54 ± 0.19 | 0.37 ± 0.10 0.38 ± 0.13 0.48 ± 0.18 |

(b) PM₂.₅ Number of data 15 13 |
| Mass  | 47.17 ± 21.57 44.03 ± 22.19 42.17 ± 18.55 | 44.09 ± 15.32 45.77 ± 15.24 45.71 ± 16.44 |
| Cl⁻   | 5.14 ± 2.68 4.91 ± 2.76 4.83 ± 3.02 | 0.81 ± 0.64 0.90 ± 0.62 0.69 ± 0.51 |
| NO₃⁻  | 9.15 ± 6.67 9.14 ± 7.16 9.10 ± 5.92 | 7.34 ± 3.20 7.53 ± 3.08 7.67 ± 3.25 |
| SO₄²⁻ | 4.81 ± 3.18 4.89 ± 3.64 4.68 ± 3.02 | 9.33 ± 4.73 10.26 ± 5.17 10.29 ± 5.42 |
| Na⁺   | 0.28 ± 0.12 0.34 ± 0.11 0.25 ± 0.08 | 0.18 ± 0.09 0.35 ± 0.15 0.49 ± 0.23 |
| NH₄⁺  | 5.52 ± 3.63 5.41 ± 3.73 5.45 ± 3.19 | 5.52 ± 2.52 5.87 ± 2.65 5.99 ± 2.77 |
| K⁺    | 0.83 ± 0.52 0.82 ± 0.52 0.79 ± 0.43 | 0.57 ± 0.25 0.69 ± 0.29 0.63 ± 0.28 |
| Mg²⁺  | 0.06 ± 0.03 0.07 ± 0.04 0.06 ± 0.03 | 0.03 ± 0.02 0.04 ± 0.03 0.04 ± 0.02 |
| Ca²⁺  | 0.29 ± 0.12 0.32 ± 0.11 0.28 ± 0.09 | 0.22 ± 0.07 0.33 ± 0.13 0.30 ± 0.10 |

Mean ± standard deviation (µg/m³).

1.8 m using the automatic weather station (AWS; Campbell 05103-L R.M. Young Wind Monitor) at a distance of 80 m from the roadside.

### 2.2 Sampling and Analysis

Samples of PM₁₀ and PM₂.₅ were collected using a low-volume air sampler with a flow rate of 16.7 L/min, which consists of one-stage Teflon filter packs and cyclones (URG-2000-30ENB, URG-2000-30EH) of cut-size 10 µm and 2.5 µm each. The sampling height was roughly 1.5 m above the surface. Samples for measuring the concentrations of total mass and ionic components in both PM₁₀ and PM₂.₅ were collected using a Teflon membrane filter (Zefluor filter) with a diameter of 47 mm. Only PM₁₀ samples were collected for measuring OC and BC concentrations using a quartz filter (Whatman 1851-047, QMA grade), because the number of filter packs was not sufficient to collect PM₂.₅ as well at three locations. Considering that OC and BC are present mostly in PM₂.₅, only PM₂.₅ could have been collected. However, PM₁₀ rather than PM₂.₅ was collected to quantify all carbonaceous particles originating from the roads, because OC and BC can be included in coarse particles such as those from tire wear (Watson et al., 1998). With regard to sampling design, installing upstream denuders and a backup filter/denuder to the filter pack can minimize positive or negative sampling artifacts (Kim et al., 2015). However, such installation is complex and labor-intensive, and was not feasible for this study. Samples were collected for 24 hours starting at 10 a.m., except in special circumstances. Teflon filters were conditioned at 40% relative humidity for 24 hours before and after the sampling and were weighed using an electronic balance (DVG215CD, Ohaus). For ion analysis, a Teflon filter, which is hydrophobic, was first soaked with ethanol in a vial to facilitate the contact with distilled water. After filling the vial with distilled water, ions were eluted using ultrasonic extractor (Power Sonic #420, Hwashin Tech). Detailed procedures for handling filters are described in Won et al. (2010) and Kim et al. (2015).
a solution of 3.5 mM Na$_2$CO$_3$ and 1 mM NaHCO$_3$ as the eluent. Cations were analyzed using Metrosep C2 150 and C4 150 columns with solutions of 4 mM HNO$_3$ and 1.7 mM HNO$_3$/0.7 mM dipicolinic acid as eluents, respectively. The minimum detection limits for the IC analysis were determined by analyzing standard solutions of minimum concentrations used for the IC calibration seven times repetitively. The values in μg/L (with uncertainties in parentheses as %) were 4.4 (2.0) for Cl$^-$, 9.8 (2.7) for NO$_3^-$, 8.1 (2.2) for SO$_4^{2-}$, 6.2 (3.1) for Na$^+$, 11.9 (6.1) for NH$_4^+$, 14.1 (5.1) for K$^+$, 10.3 (3.6) for Mg$^{2+}$, and 5.3 (6.5) for Ca$^{2+}$.

A quartz filter for OC and BC analysis was used after baking overnight at 450°C. Samples collected by filters were sent to the Center for Air Resources Engineering and Science (CARES) at Clarkson University, Potsdam, New York, United States, where OC and BC were analyzed by the National Institute of Occupational Safety and Health (NIOSH) Method 5040 using thermal-optical transmittance (TOT).

3. RESULTS AND DISCUSSION

3.1 Meteorology and Number of Samples

One of the most important factors when investigating the effects of road vehicles on ambient air quality is wind direction. Air pollutant concentrations vary considerably depending on whether the measurement location is upwind or downwind (Zhu et al., 2002a). However, calm winds (less than 0.5 m/s) predominated throughout the study periods, accounting for 61 and 87% of the time in January and May, respectively. Northerly wind, which blew along the north-south running road, accounted for 30% in January and 7.2% in May. Although average wind speed from the north was high compared with that from other directions, it was merely 1.19 ± 0.50 m/s and 1.58 ± 0.90 m/s in January and May, respectively. In other words, wind direction and speed were not significant factors in this study.

Because only wind direction and speed data were collected at the measurement site, other meteorological data were taken from the nearest weather station, which is located about 22 km to the east-southeast. During the study periods, average temperature was −2.0°C (ranging from −8.4 to 2.0°C) in January and 17°C (ranging from 11 to 23°C) in May. Fig. 2 shows variations of 24-hour average PM$_{10}$ and PM$_{2.5}$ concentrations over the study periods. In January, three occasions of precipitation, including a heavy snow on the 11th, occurred, and there was a relatively large amount of rainfall in May.

Table 1 summarizes the measurement results during the study periods. Samples were collected for 20 days from January 4 to 24. In January, the total number of samples was 16 for PM$_{10}$ and 15 for PM$_{2.5}$, which fell 4 and 5 short of a possible maximum of 20, respectively. For one set of measurements, nine filters, which consisted of three Teflon filters and three quartz filters for PM$_{10}$ and three Teflon filters for PM$_{2.5}$, were collected at three measurement locations. If any one of the nine samples was missing during the sampling and analysis process, all samples for those measurements were excluded. Another reason for the reduced number of data was due to collecting samples for 48 hours; a heavy snow on January 11 made it difficult to access the measurement site (Fig. 2(a)).

Initially, we considered not collecting samples in the presence of precipitation. However, we continued taking measurements because it was believed that the effects of precipitation on fugitive dust generation could be large and thus worth checking (Choi et al., 2014). However, variations in concentrations with distance...
did not change significantly due to precipitation, even on January 11 through 13 when significant amounts of snow piled up.

3.2 Variations in Concentrations with Distance from the Roadside

Fig. 3 shows variations in concentrations of PM, BC, and OC with distance from the roadside. In January, relative concentrations of PM$_{10}$ and PM$_{2.5}$ at 200 m were 0.83 and 0.89, respectively, compared with their concentrations at 10 m. Furthermore, the relative concentration of PM$_{10}$ at 80 m was 0.79, which is slightly less than that at 200 m. As pointed out previously, a decrease in PM$_{10}$ concentrations with distance is relatively small compared with BC or OC, for which vehicle exhaust accounts for the majority of total emissions (Zhu et al., 2002a, b; Roorda-Knape et al., 1998). As shown in Fig. 3, PM$_{10}$ concentrations at 200 m increased compared with those at 80 m, albeit there was a relatively small sample size at the three measurement locations. PM$_{10}$ concentrations at 80 m were lower than those at 200 m in May as well, as in January. However, relative concentrations were generally higher, and PM$_{2.5}$ concentrations at both 80 m and 200 m were higher than those at 10 m. If concentrations at 10 m accurately represent the effects of vehicle emissions, then effects other than vehicle emissions were greater for PM$_{2.5}$ than for PM$_{10}$, and greater in May than in January.

As in Zhu et al. (2002a), relative concentrations of BC, a greater proportion of which is emitted from vehicle exhausts, were lower than those of PM$_{10}$ and PM$_{2.5}$ at 200 m in Fig. 3. However, relative concentrations of BC at both 80 and 200 m in January were higher than those in May, which shows that the effects of emissions other than vehicle emissions were relatively large in January. Relative concentrations of OC with a variety of emission sources were larger than those of BC; the small differences in relative concentrations between January and May denote a small seasonal influence.

3.3 Primary Factors of Concentration Variations

Fig. 4 shows variations in major ion concentrations of PM$_{10}$ and PM$_{2.5}$ in January. SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ were used to represent secondary products, and Ca$^{2+}$, K$^+$, and Cl$^-$ were used as markers of crustal component, biomass burning, and open burning, respectively (Watson et al., 1998). Although Cl$^-$ is generally known to be a tracer of sea salt, a correlation coefficient of −0.01 between Cl$^-$ and Na$^+$ and a high equivalent ratio of Cl$^-$/Na$^+$ at 5.95 (from both PM$_{10}$ and PM$_{2.5}$) suggests that the origin of Cl$^-$ is other than sea salt and presumed to be open burning (Table 1).

In January, PM$_{10}$ concentrations were higher at 200 m than at 80 m, and OC and BC concentrations decreased gradually with distance from the roadside (Fig. 3). However, all ion concentrations were higher at 200 m than at 80 m, as in Fig. 4. Compared with concentrations at 10 m, Ca$^{2+}$ (a tracer of crustal component) de-
increased more rapidly than other ions, but a slight decrease in K\(^{+}\) (a tracer of biomass burning) occurred. In other words, the effects of biomass burning are considered to be greater than fugitive dust from surrounding areas beyond 200 m. However, the reason for the highest K\(^{+}\) concentration in PM\(_{10}\) at 10 m is unclear.

In Table 2, correlations between total mass, OC, and BC and ions were examined for PM\(_{10}\) and PM\(_{2.5}\), and for January and May. Correlations of OC and BC in PM\(_{2.5}\), which were not measured, were calculated using OC and BC in PM\(_{10}\). This was based on the assumption that most OC and BC exists in PM\(_{2.5}\), although some OC and BC from tire and brake wear can exist in coarse particles (Watson \textit{et al.}, 1998). As in Table 2(a), correlation of total mass is the highest with K\(^{+}\), high with NO\(_3\)\(^{-}\), NH\(_4\)\(^{+}\), and Cl\(^{-}\), and not as high with Ca\(^{2+}\) in the case of PM\(_{10}\) in January. This corroborates that the primary causes of variations in PM\(_{10}\) are biomass

### Table 2. Correlation coefficients between total mass, OC, and BC and ions in PM\(_{10}\) and PM\(_{2.5}\),

|       | PM\(_{10}\)          | PM\(_{2.5}\)          |
|-------|----------------------|----------------------|
|       | Total mass | OC | BC | Total mass | OC\(^{b}\) | BC\(^{b}\) |
| (a) January |  |  |  |  |  |  |
| NO\(_3\)\(^{-}\) | 0.89\(\ast\ast\) | 0.66\(\ast\ast\) | 0.59\(\ast\ast\) | 0.86\(\ast\ast\) | 0.45\(\ast\ast\) | 0.31\(\ast\) |
| SO\(_4\)\(^{2-}\) | 0.72\(\ast\ast\) | 0.41\(\ast\ast\) | 0.27 | 0.79\(\ast\ast\) | 0.22 | -0.05 |
| NH\(_4\)\(^{+}\) | 0.88\(\ast\ast\) | 0.65\(\ast\ast\) | 0.57\(\ast\ast\) | 0.89\(\ast\ast\) | 0.44\(\ast\ast\) | 0.26 |
| Ca\(^{2+}\) | 0.41\(\ast\ast\) | 0.20 | 0.32\(\ast\) | 0.58\(\ast\ast\) | 0.25 | 0.37\(\ast\) |
| K\(^{+}\) | 0.91\(\ast\ast\) | 0.66\(\ast\ast\) | 0.60\(\ast\ast\) | 0.92\(\ast\ast\) | 0.38 | 0.28 |
| Cl\(^{-}\) | 0.79\(\ast\ast\) | 0.70\(\ast\ast\) | 0.75\(\ast\ast\) | 0.73\(\ast\ast\) | 0.53\(\ast\ast\) | 0.58\(\ast\ast\) |
| (b) May |  |  |  |  |  |  |
| NO\(_3\)\(^{-}\) | 0.75\(\ast\ast\) | 0.36 | 0.29 | 0.63\(\ast\ast\) | 0.20 | 0.27 |
| SO\(_4\)\(^{2-}\) | 0.75\(\ast\ast\) | 0.30 | 0.23 | 0.76\(\ast\ast\) | 0.23 | 0.35 |
| NH\(_4\)\(^{+}\) | 0.79\(\ast\ast\) | 0.35 | 0.31 | 0.79\(\ast\ast\) | 0.28 | 0.40\(\ast\) |
| Ca\(^{2+}\) | 0.80\(\ast\ast\) | 0.51\(\ast\ast\) | 0.30 | 0.47\(\ast\ast\) | 0.48\(\ast\) | 0.32 |
| K\(^{+}\) | 0.71\(\ast\ast\) | 0.49\(\ast\ast\) | 0.25 | 0.78\(\ast\ast\) | 0.52\(\ast\ast\) | 0.52\(\ast\ast\) |
| Cl\(^{-}\) | 0.15 | 0.63\(\ast\ast\) | 0.48\(\ast\ast\) | 0.40\(\ast\) | 0.58\(\ast\ast\) | 0.53\(\ast\ast\) |

\(^{a}\) Student's \(t\)-test: \(\ast p<0.05\), \(\ast\ast p<0.01\).

\(^{b}\) Used OC and BC values in PM\(_{10}\).

### Fig. 4. Variations in concentrations of primary ions in PM\(_{10}\) and PM\(_{2.5}\) with distance from the roadside in January. Meanings of symbols and error bar are the same as in Fig. 3.
burning, open burning, and secondary formation rather than fugitive dust. Considering that \( K^+ \) and \( Cl^- \) were highly correlated with OC and BC, gradual declines of OC and BC are related to biomass and open burning in Fig. 3.

Fig. 3 shows a decrease of PM\(_{2.5}\) in January, but there is no discernible trend except a high Ca\(^{2+}\) concentration at 80 m in Fig. 4. Because of differences in variations of Ca\(^{2+}\) and PM\(_{2.5}\) mass, Ca\(^{2+}\) has the weakest correlation with total mass. Despite a higher correlation between secondary ions and total mass in Table 2(a), there are no distinct variations with distance in Fig. 4, which can be explained by the fact that the secondary formation on the road and in surrounding areas is similar.

It is highly likely that a decrease of PM\(_{2.5}\) is primarily due to OC and BC, if variations in ions fail to support a decrease of PM\(_{2.5}\) in January (Fig. 3). As shown in Table 1, PM\(_{2.5}\) concentration at 200 m is 5 \( \mu g/m^3 \) lower than that at 10 m, but OC and BC concentration in PM\(_{10}\) at 200 m is 2.62 \( \mu g/m^3 \) lower than that at 10 m. In contrast, the ion sum is smaller by only 0.64 \( \mu g/m^3 \). Despite the use of OC and BC in PM\(_{10}\), it is sufficient to verify the effects of OC and BC in a decrease of PM\(_{2.5}\) considering that most of OC and BC are present in PM\(_{2.5}\).

Even in May, secondary ions exhibited small variations, as shown in Fig. 5. However, secondary ions in PM\(_{2.5}\) increased with distance, similar to variations of PM\(_{2.5}\) in Fig. 3, showing that variations of PM\(_{2.5}\) are associated with secondary ions. However, a correlation between total mass and secondary ions is lower than that in January. It is interesting to note that mass concentrations exhibited a significant correlation with NH\(_4^+\) and NO\(_3^-\) in January but with NH\(_4^+\) and SO\(_4^{2-}\) in May. It is generally known that NO\(_3^-\) is primarily influenced by local effects while SO\(_4^{2-}\) is more influenced by regional effects (Edgerton et al., 2006; Brook et al., 2002). Different correlations of NO\(_3^-\) and SO\(_4^{2-}\) in January and May should also have resulted from the influence of surrounding areas rather than the influence of roads, but further study is warranted to confirm the current assertion.

Compared with that in January, a higher correlation with Ca\(^{2+}\) in PM\(_{10}\) is noteworthy in May. Substantial fugitive dust generation can be seen to occur at 200 m more affected by surrounding areas in May with a higher temperature than in January with a lower temperature below freezing. However, absolute concentrations of Ca\(^{2+}\) were higher at 10 m as well as at 200 m in January than in May (Table 1).

Fig. 6 shows the correlation between OC and BC. It is presumed that a larger slope in January than in May is due to the influence of biomass burning and open burning, which emit more OC than vehicle exhaust. It can also be interpreted that the largest slope at 200 m
Particulate Matter near a Major Road in Korea

39

in January is associated with emissions from biomass and open burning. As pointed out previously, the influence of secondary formation is significant in May, thereby causing a small variation of slope with distance (standard deviation of 0.34 compared with 0.59 in January) and less steep slopes than in January.

Fig. 7 shows average composition variations of PM$_{10}$ and PM$_{2.5}$ with distance. In January, an abundance of primary ions, OC, and BC confirms again the importance of biomass or open burning in variations of PM. In May, considerable amounts of secondary ions and others exist in both PM$_{10}$ and PM$_{2.5}$. As photochemical reactions become active due to temperature rise, the influence of secondary formation increased in PM$_{10}$ as well as PM$_{2.5}$, leading to decreased variations with distance.

4. SUMMARY AND CONCLUSION

For about 20 days each in January and May 2008, particle-phase concentrations were measured at three distances of 10, 80, and 200 m from the roadside of National Highway 45, which runs in front of the Global Campus of HUFS, located about 35 km southeast of downtown Seoul. The highway has two lanes each way, with an average hourly traffic volume of 1,070 vehicles. Considering that calms (defined as less than 0.5 m/s) accounted for 61% and 87% in January and May, respectively, the wind is considered to be of little importance.
In January, PM\(_{10}\) concentrations were lowest at 80 m. An increase in PM\(_{10}\) at 200 m was considered to result from the influence of biomass burning and open burning, while the influence of fugitive dust was less evident. A decrease of BC concentration became relatively small due to the influence of biomass and open burning from surrounding areas. Secondary formation varied a little with distance; this trend is more pronounced for PM\(_{2.5}\). In May as well, PM\(_{10}\) concentrations were the lowest at 80 m. However, PM\(_{10}\) concentrations had little variation compared with those in January, and PM\(_{2.5}\) concentrations tended to increase with distance. It was acknowledged that fugitive dust and secondary formation play an important role in variations of PM\(_{10}\) and PM\(_{2.5}\), respectively. The influence of secondary formation increased in PM\(_{10}\) as well as in PM\(_{2.5}\), leading to decreased variations with distance.

This study demonstrated that the influence of vehicle emissions on PM mass concentrations is limited even near the roadside. To reduce PM mass concentrations in the vicinity of the road, not only vehicle emissions but also other major emission sources, such as biomass burning, open burning, and fugitive dust, as well as secondary formation, should be managed comprehensively as in other atmospheric environment.

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