보건학석사 학위 논문

Spatial variability of $PM_{2.5}$ measured using compact filter-based sampler in Seoul, Korea

필터 기반 소형 샘플러를 이용한 서울시 $PM_{2.5}$의 공간적 변이에 관한 연구

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Abstract

Spatial variability of $PM_{2.5}$ measured using compact filter-based sampler in Seoul, Korea

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There was good evidence of the association between exposure to $PM_{2.5}$ and human health relying on spatial contrast. Because regulatory monitoring networks were not established for epidemiological studies, regulatory monitoring data may not well estimate exposures to air pollution across people's residences for assessing health effects. To better characterize spatial variability of $PM_{2.5}$, a two-week community monitoring campaign was performed three times during August 2015 to August 2016 in different seasons at 19 sampling sites of 5 district areas in Seoul using Deployable Particulate Impact Sampler (DPIS).

Prior to apply DPIS to monitoring campaign, its performance was evaluated by comparing to Low-volume Cyclone Sampler (LCS) which has been consistently provided $PM_{2.5}$ data since 2003 in the Seoul National University Yeongeon campus, Seoul, Korea. Using a duplicated DPIS, the reliability of DPIS was confirmed by computing relative precision and mean square error-based R squared value (R^2). Relative precision was one minus the difference of measurements

between two samplers relative to the sum. For accuracy, $PM_{2.5}$ concentrations from two DPISs (DPIS_T and DPIS_Q) were compared to those of LCS. Two samplers included two types of collection filters (Teflon, T; quartz, Q). We assessed accuracy using accuracy value which is one minus the difference between DPIS and LCS $PM_{2.5}$ relative to LCS $PM_{2.5}$ in addition to MSE-based R^2. DPIS showed high reliability (average precision = 97%, R^2 = 0.98). Accuracy was generally high for all DPISs (average accuracy = 87-89%, R^2 = 0.91). To determine the differences according to measurement method, LCS and beta-ray attenuation method (BAM) were compared and they were significantly different (t value = -9.0) especially in high-level mass concentrations.

In the result of measuring $PM_{2.5}$ by DPIS in community monitoring campaigns, the average mass concentrations ranged from 25.4 to 46.1 μg/m^3 across the sampling sites and different seasons. Wintertime levels peaked at congested sites in southwest and central area under atmospheric stability conditions. Conversely, summertime concentrations were generally low relative to winter especially at sites nearby urban park in southwest and southeast area. Chemical component proportions of $PM_{2.5}$ revealed that $PM_{2.5}$ at 19 sampling sites in Seoul consisted of 18-22% OC, 3-4.1% EC, 8-9.5% nitrate, 17.5-20.6% sulfate and 9-10% ammonium, on an average basis of total sampling period. Organic carbon (OC), a major constituent of $PM_{2.5}$, exhibited relatively high concentrations in winter particularly at sites affected by ambient sources such as incineration facility and charcoal fire emission of restaurants in northwest and southwest area. On the contrary, elemental carbon (EC) didn't show consistently high level sites over the season, indicating it was not contributed to stationary sources but traffic emissions. Among secondary ions, nitrate was extremely peaked in wintertime under the particle formation favored by condensation of cold temperature. Moreover, ionic balance indicated overall neutral $PM_{2.5}$ aerosols close to slightly acidic. Correlation between components varied between sites, but generally high between ammonium and sulfate (average r = 0.76). Despite the high correlation between ammonium and nitrate (average r = 0.63), it varied across the sites (0.57-0.86) and some nitrate concentrations in several sites showed high correlation with OC rather than ammonium.

For spatial variability of $PM_{2.5}$ measurements in Seoul, coefficient of spatial variation (CV) and coefficient of divergence (COD) was computed across the sites. Consequently, EC and nitrate, which are mainly attributed to diesel emissions, were distributed unevenly in spatial patterns relative to other components.

This study provides the knowledge of spatial characteristics of $PM_{2.5}$ data measured at 19 sampling sites in Seoul, Korea. The standardized measurement of $PM_{2.5}$ using evaluated sampler, DPIS, across Seoul will contribute to a consistent assessment of individual exposure level to $PM_{2.5}$ in further health effect studies.

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Keywords : $PM_{2.5}$, cost-effective sampler, reliability, accuracy, component distribution, spatial variability, Seoul

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1. Introduction

1.1 Background

A considerable number of previous epidemiological studies has been reported the association between exposure of particulate matter (PM) less than 2.5 μm in aerodynamic diameter, $PM_{2.5}$, and adverse human health effects such as diseases of respiratory and cardiovascular system, lung cancer, increasing in premature mortality and so on (Atkinson et al., 2014; Pope et al., 2011; Turner et al., 2011; Franklin et al., 2007; Pope and Dockery, 2006). To demonstrate direct causality with $PM_{2.5}$ and health effect, the cohort study aimed individuals is necessary. The dominant approach for determining exposure to $PM_{2.5}$ in cohort studies is the estimation of individual exposure level in study area by developing prediction model using $PM_{2.5}$ measurements at one site in national monitoring network. However, these approach could occur difficulties resulted in a limited number of monitoring sites (Hoek et al., 2008; Jerrett et al., 2005).

The exposure level of the individuals over a long term period could be mainly caused differences by spatial contrasts of $PM_{2.5}$ primarily affected by ambient source emissions in local scale rather than temporal variation. Thus, within-city spatial variability of $PM_{2.5}$ should be ascertained prior to using measurements as a predicted value in order to prevent misinterpretation of $PM_{2.5}$ spatial variations possibly be leading the uncertain outcome of long-term cohort epidemiological studies (Szpiro et al., 2011, 2010; Wilson et al., 2005; Pinto et al., 2004). Based on the importance of identifying the spatial variability of $PM_{2.5}$, previous foreign studies performed spatial monitoring campaigns supplementary to existing regulatory monitoring network to better represent spatial variability of $PM_{2.5}$ across people's residences (Eeftens et al., 2012; Cohen et al., 2009). However, they have not been implemented in the country.

The city of Seoul is one of the most densely populated in the world with large volume of traffic and has a topographic characteristic of basin impeding diffusion of air pollutants. Also, a metropolitan area like Seoul could have a complicated emission source of air pollutants (Heo et al., 2009), thus there is a high probability of showing significant intra-urban spatial contrasts of $PM_{2.5}$. These $PM_{2.5}$ spatial variabilities are largely affected by its chemical components, such as organic compounds and secondary ions, which vary depending on their sources in their proportion (Bell et al., 2007). The chemical components of $PM_{2.5}$ have important association with adverse health impacts, which is indicating that mass alone is not a sufficient index to evaluate health effects of $PM_{2.5}$ exposures (Rohr and Wyzga, 2012; Franklin et al., 2008). Nonetheless, there have currently been operated 25 urban air pollution monitoring sites in Seoul, Korea, which are located only one site in respective 25 districts of Seoul bring about difficulty to represent residents' exposure level in each districts. Therefore, the need of increasing spatial measurements for $PM_{2.5}$ mass and its component concentrations in Seoul arises.

The higher spatial resolution of $PM_{2.5}$ is required to assess better representative of individual exposure level, but the high costs associated with conventional measurements limit the number of air quality monitoring sites, leading to difficulty in obtaining spatially-defined air quality information (Johnson et al., 2016). Also, differences in site selection and differences of sampling and analysis method make it harder to interpret of spatial contrasts of $PM_{2.5}$ (Eeftens et al., 2012). In other words, a cost-effective compact sampler using identical sampling protocol is required for measuring $PM_{2.5}$ in spatial scale. Moreover, it was a first attempt to measure $PM_{2.5}$ concurrently in spatial scale using gravimetric method in Seoul, Korea. Therefore, this study focused on the foundation design for $PM_{2.5}$ spatial sampling using cost-effective filter-based sampler including the evaluation of sampler performance, in addition to the result of the sampling.

1.2 Objectives

The aim of this study is to establish the foundation of spatial sampling for $PM_{2.5}$ including selection of suitable sampler and evaluation its performance. A second aim is to assess the spatial distribution and variability of $PM_{2.5}$ mass concentrations as well as chemical components in Seoul, Korea measured by standardized spatial monitoring campaigns using evaluated $PM_{2.5}$ samplers.

2-1. Method of sampler performance evaluation

2-1.1 Description of samplers

The $PM_{2.5}$ could be measured by rays which is continuous measurement, or filter-based method. A sort of the former case, beta-ray attenuation method (BAM), is used in regulatory monitoring network in Seoul, Korea. In the latter case, the gravimetric method which is determined the particle mass concentration by weighing the filters before and after sampling, has been verified to attain stable measurements rather than other methods (U.S. EPA, 2006). The gravimetric values could be measured by two of elutriators divided into impactor and cyclone according to the principle of eliminating coarse particles larger than 50% cut-off point diameter of particulate matters. Unlike cyclone, impactor doesn't require separate devices because impactor is inside a sampler. Thus, impactor has generally more compact relative to a cyclone (National Research Council, 2005).

The inertial impactor sampler using in this study, Deployable Particulate Impact Sampler (SKC Inc., USA, U.S. Patent No. 7,334,453, hereafter referred as DPIS) which has light-weight and compact design (specification: 7×5×10 cm, weight: 0.23 kg) was qualified by comparing to other

compact sampler (Patterson et al., 2010). However, those compact samplers have lack of base data for their performance (Baldauf et al., 2001), thus it is required to evaluate of sampler performance through comparing with validated sampler used in numerous studies (Chen et al., 2011; Gupta et al., 2011; Case et al., 2008). To validate performance of DPIS, a Low-volume Cyclone Sampler (URG corp., USA, hereafter referred as LCS) is used as standard sampler, which has been normally used in earlier studies for particulate matter (Lee et al., 2015a; Joly et al., 2010; Park et al., 2007; Jetter et al., 2002). LCS used in this study is composed of filter pack (URG-2000-30FG, URG corp., USA) and cyclone (URG-2000-30EH, URG corp., USA). It has operated at a fixed site in the Seoul National University Yeongeon campus, Seoul, Korea since 2003 and provided qualified $PM_{2.5}$ data (Heo et al., 2014; Heo et al., 2009; Kim et al., 2007). The flow rate required to sustain 50% cut-off point aerodynamic diameter of 2.5 μm is 16.7 L/min for LCS, and 10 L/min for DPIS. The structure of samplers (DPIS, LCS and BAM-1020) is shown schematically in Fig. 1.

2-1.2 Evaluation of sampler performance

The method of investigation for sampler performance such as reliability and accuracy focused on measuring $PM_{2.5}$ mass concentration was described in the following sections. To evaluate of sampler performance, side-by-side comparison sampling was conducted during September 2015 to February 2016 at urban area in Seoul (Seoul National University Yeongeon campus, 37.58° N, 127.00° E, 17 m above ground) using DPIS and LCS. The sampling period is separated that first period was for reliability of DPIS during September 2015 to January 2016, and second period was for estimating precision of DPIS during January to February 2016. Because LCS measures $PM_{2.5}$ to determine mass concentrations using 47 mm Teflon filter with a polymethylpentene (PMP) support ring (1.0 μm pore size, Pall Life Sciences, USA), the identical filter was applied

to DPIS and furthermore, quartz microfiber filter (Whatman, UK) was in addition to DPIS for further availability of components analysis especially for carbon. As shown in Fig. 1 (a), two of DPIS named according to sample filters as DPIS_T and DPIS_Q (Teflon and quartz filter, respectively) were used in comparison sampling. Both samplers used greased porous plastic pads as an impactor. The methods of sampling and sample measurements were described in section 3-1.3 and 3-1.4.

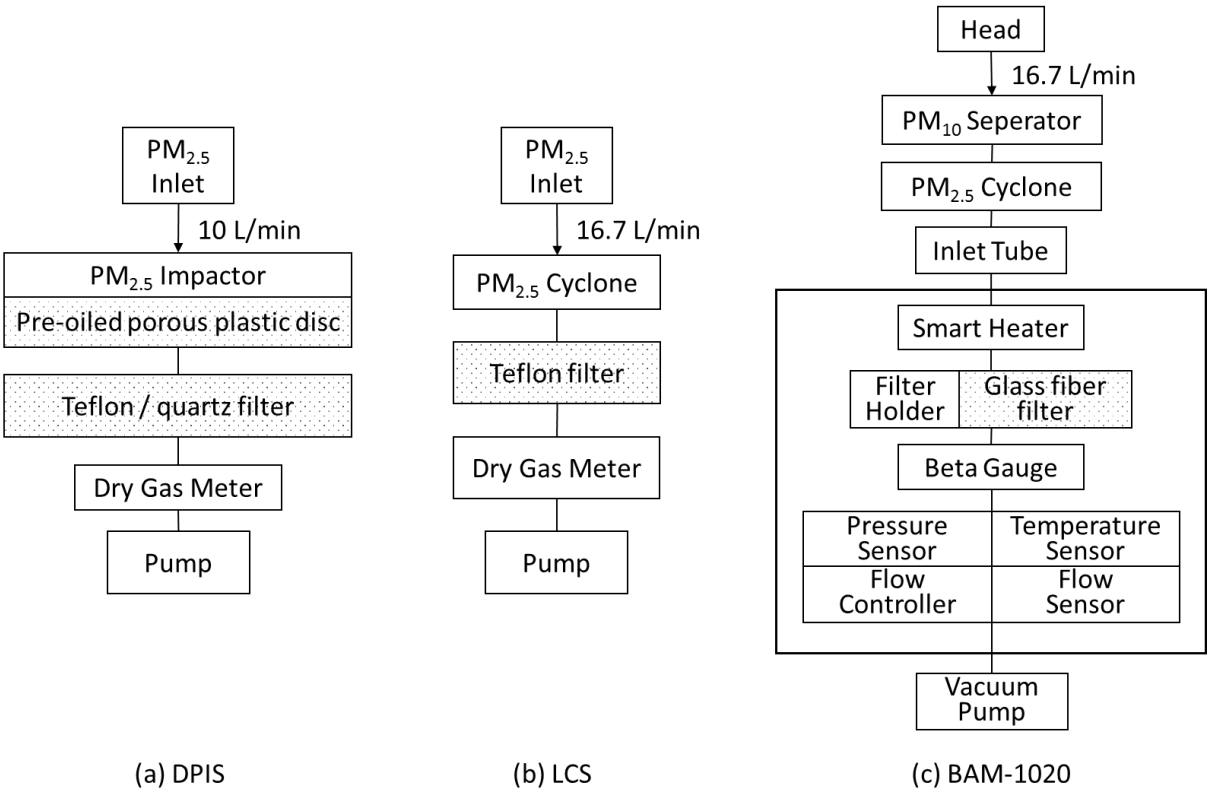

Figure 1. The schematic of three samplers: (a) Deployable Particulate Impact Sampler (DPIS) with different filters (Teflon and quartz); (b) Low-volume Cyclone Sampler (LCS); (c) BAM-1020 in the government air quality monitoring network.

2-1.2.1 Reliability of DPIS

To investigate the reliability of DPIS, comparative measurement was performed between two of identical samplers included quartz filter (DPIS_Q) arranged side-by-side. The other sampler which has identical condition with DPIS_Q was named DPIS_Qd. Using a duplicated DPIS, reliability of DPIS was confirmed by computing relative precision (RP). It was defined by one minus the difference of measurements between two samplers relative to the sum, and it was obtained with following equation (chen et al., 2011).

$$\text{RP}\ (\%) = \left(1 - \frac{|\text{DPIS}_\text{Q} - \text{DPIS}_\text{Qd}|}{\text{DPIS}_\text{Q} + \text{DPIS}_\text{Qd}}\right) \times\ 100 \qquad (1)$$

Based on equation (1), it can be inferred that DPIS has high reliability as RP value increases. Also, correlation between DPIS_Q and DPIS_Qd was visually confirmed by create scatter plot. Afterwards, mean square error (MSE)-based coefficient of determination (R^2) with fitted regression line was calculated to confirm consistency between measurements of two samplers. The MSE-based R^2 compared observations based on identity line while R^2 using correlation coefficient compared measurements on the basis of regression line (Kim et al., 2016; Keller et al., 2015). The purpose of this section is investigation for consistency, thus MSE-based R^2 was used in this study.

2-1.2.2 Accuracy of DPIS

The measurements of DPIS_T and DPIS_Q were compared to LCS measurements to determine accuracy of DPIS. It could be presented as correspondence (CP) to LCS, which is defined as follows (chen et al., 2011):

$$CP\ (\%) = \left(1 - \frac{|T-m|}{T}\right) \times 100 \quad (2)$$

where T is true value and m is measured value in this equation. This study assumed that LCS measurement is true value, regard as T, and m was substituted to respective observations of DPIS_T and DPIS_Q. Alike estimation of reliability, high value of CP indicates the high accuracy of DPIS. MSE-based R^2 for accuracy was also computed to identify the extent of correspondence to LCS.

2-1.3 Comparison between BAM and gravimetric method

The concentration of $PM_{2.5}$ could vary widely with the measurement method due to equipment used for measuring particles, which affected by ambient environment (Amaral et al., 2015). The regulatory air pollution monitoring sites in Seoul is operating for measuring $PM_{2.5}$ using BAM of Met One, Inc. (Model 1020, Met One Instruments Inc., USA, hereafter referred as BAM-1020), which also probably cause differences with gravimetric method. Therefore, gravimetric sampler, LCS, was compared to BAM-1020 in nearest national monitoring station 1.08 km away from LCS to estimate the differences between them. The comparison data was 24-hour average measurements of BAM-1020 and integrated 24-hour samples of LCS during January 2015 to December 2016 (N=332). The high and low tendency between them was expressed as the Pearson correlation coefficient (r) determined using SPSS (version 22.0, IBM Corp., USA). Also using SPSS, a paired *t*-test was performed to determine differences according to concentration ranges measured by LCS as follows: below 25 μg/m^3 (low level), between 25 ~ 50 μg/m^3 (intermediate level), and more than 50 μg/m^3 (high level).

2-2. Result and discussion of sampler performance evaluation

2-2.1 Evaluation of sampler performance

The number and statistical summary of values measured by respective DPIS types are presented in Table 1. DPIS_Q and DPIS_Qd installed for investigating reliability of DPIS showed closely similar $PM_{2.5}$ mass concentrations each other (40.7 ± 17.2 μg/m^3 and 40.3 ± 17.1 μg/m^3, respectively). In the comparative sampling to LCS for determining accuracy of DPIS, the average mass concentration of DPIS_T and DPIS_Q (29.9 ± 13.7 μg/m^3 and 30.3 ± 16.6 μg/m^3, respectively) had approximate value to LCS (32.0 ± 16.0 μg/m^3). More detailed about evaluation reliability and accuracy of DPIS is in the following sections.

Table 1. Summary statistics of 24-hour $PM_{2.5}$ concentrations collected by LCS and four DPIS with different filters at one monitoring site in the Seoul National University Yeongeon campus, Seoul.

Sample purpose	Sampler	N	Minimum (μg/m^3)	Median (μg/m^3)	Maximum (μg/m^3)	Average ± SD (μg/m^3)
Reliability	DPIS_Q	15	9.18	47.94	61.01	40.70 ± 17.18
	DPIS_Qd	15	9.87	47.54	59.98	40.34 ± 17.06
Accuracy	LCS	9	14.20	24.58	67.88	31.99 ± 15.98
	DPIS_T	9	11.91	26.98	58.52	29.94 ± 13.72
	DPIS_Q	9	11.04	26.65	65.29	30.32 ± 16.58

DPIS = Deployable Particulate Impact Sampler, LCS = Low-volume Cyclone Sampler.

2-2.1.1 Reliability of DPIS

In the equation (1), the average of RP was resulted in the calculation as 97.28% indicating as high reproducibility. Also the result of linear regression, two of identical DPIS were well fitted in one-to-one line and high consistency was shown as 0.98 of MSE-based R^2 adding on to the regression line slope of 0.999 (Fig. 2).

Although U.S. EPA suggests that triplicated samplers were required as a condition for demonstration as federal equivalent sampler comparable to federal reference sampler (U.S. EPA, 2002), this study performed the comparative sampling for reliability estimation using duplicated sampler. This is because duplicated sampler used in this study can meet the requirements for reliability measurements and moreover it was applied to various studies (Chen et al., 2011; Hyslop et al., 2009; Smargiassi et al., 2005).

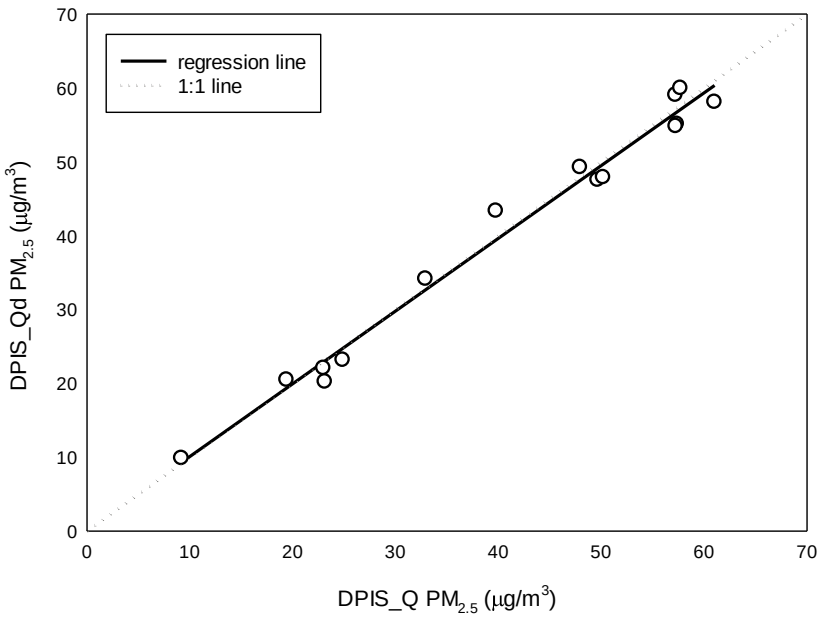

Figure 2. Scatter plot of 24-hour $PM_{2.5}$ concentrations collected by two duplicated DPISs with quartz filters (DPIS_Q and DPIS_Qd).

2-2.1.2 Accuracy of DPIS

On the whole, both DPIS_T and DPIS_Q revealed relatively high accuracy (89% and 87%, respectively) as shown in Table 2. The regression line between DPIS and LCS was also well fitted to one-to-one line especially in DPIS_Q (Fig. 3). Even though DPIS_T was rather underestimated particularly in high mass concentration according to the slope and y-intercept of regression line (0.8 and 3.4, respectively), consequently it had the closest measurements compared to LCS considering higher accuracy and lower root mean square error (RMSE) with LCS relative to DPIS_Q (4.6 and 6.4, respectively). Meanwhile, the tendency of LCS measurements was more similar with DPIS_Q than DPIS_T due to the slope of regression line close to 1 and y-intercept relatively close to 0 (0.99 and -1.4, respectively).

In this study, DPIS_Q showed a possibility of analysis of carbon, the major component of $PM_{2.5}$, through comparatively high consistency of DPIS with LCS. The particulate carbon is known as a main pollutant emitted from vehicle fuel combustion including gasoline and diesel (U.S. EPA, 2005), and be known to influence adverse effect in human health as reported in previous studies (Atkinson et al., 2015; Lippmann, 2014). Although a quartz filter is universally used for carbon analysis, not measuring the weight, because of its hydrophilic property and easily damaged material relative to Teflon filter, it could be the cost-effective alternative to measuring mass concentration and component analysis of $PM_{2.5}$ using minimal samplers. The existing relative study reported that quartz filters are also able to get reliable mass concentrations on the base of enough caring to handle it (Chartier and Weitz, 1998). Therefore, DPIS applied of quartz filter could be contributed to the assessment of people's individual exposure to $PM_{2.5}$ in extensive spatial monitoring campaigns.

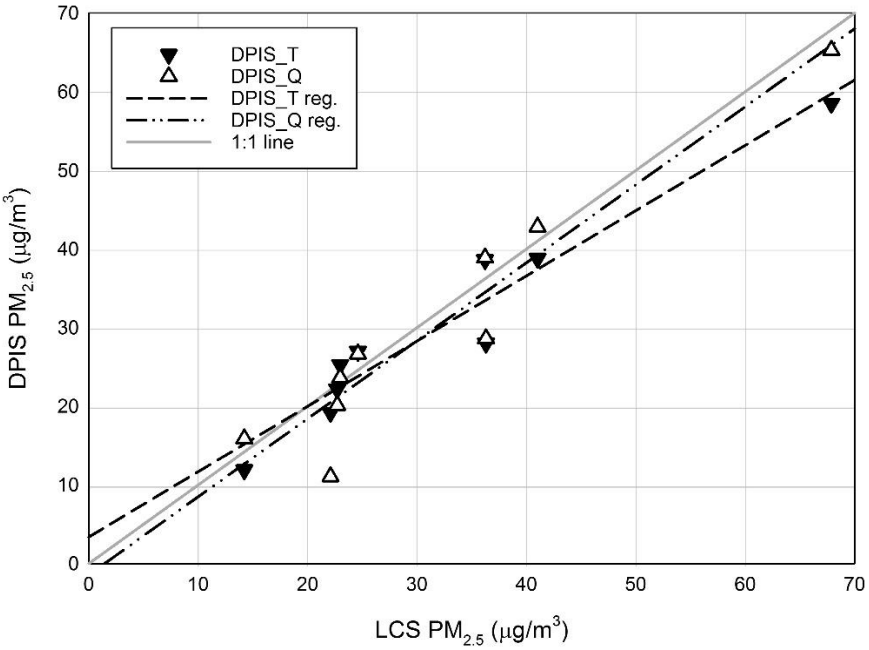

Figure 3. Scatter plot of 24-hour $PM_{2.5}$ concentrations collected by DPIS with different filters (DPIS_T and DPIS_Q) compared to LCS (dotted lines for regression lines).

Table 2. Accuracy, regression slope and intercept, and MSE-based R^2 of DPIS with different filters compared to LCS.

Sampler	Average accuracy (%)	slope	y-Intercept	MSE-based R^2	RMSE
DPIS_T	88.88	0.83	3.36	0.91	4.62
DPIS_Q	86.53	0.99	-1.42	0.91	6.40

MSE-based R^2 = Mean Square Error based R^2, RMSE = Root Mean Square Error, DPIS = Deployable Particulate Impact Sampler, LCS = Low-volume Cyclone Sampler.

2-2.2 Comparison between BAM and gravimetric method

As shown in Table 3, overall $PM_{2.5}$ mass concentrations measured by gravimetric sampler, the means of LCS and BAM-1020 measurements were different according to a *t* value of −9.0 despite a moderate correlation coefficient between them (0.63). In case that LCS had both intermediate and high mass concentrations, BAM-1020 measurements were generally underestimated relative to LCS extremely in high concentrations over 50 μg/m^3. Also means of BAM-1020 and LCS measurements were significantly different in those level having a *t* value range of −8.6 to −8.2. On the contrary, average differences between LCS and BAM-1020 were not exhibited with a *t* value of 1.8 when LCS has low concentrations under 25 μg/m^3, though a *t* value was not statistically significant with over 0.05 of *p* value. In addition, the relatively high correlation coefficient in low level (0.67) between LCS and BAM-1020 indicates that measurements of LCS and BAM-1020 had high consistency under 25 μg/m^3 of $PM_{2.5}$ mass concentrations. Nevertheless, it can be reflected that $PM_{2.5}$ mass concentrations measured by BAM was overall underestimated relative to gravimetric measurements of LCS. The underestimation of BAM could be explained by the inlet heater for reducing the moisture content of the sampled air, may leading to evaporation of semi-volatile species such as ammonium nitrate (Hauck et al., 2004). However, it should be recognized that LCS and BAM (located about 1.08 km southeast of LCS) were not compared side-by-side, so the differences in distance and ambient emission sources could affect the measurement differences between LCS and BAM. Therefore, it would be required additional side-by-side comparative sampling between gravimetric sampler and BAM to develop correction values for further health effect studies using encompassed data of both DPIS and BAM.

Table 3. Paired *t*-test comparisons of $PM_{2.5}$ mass concentrations (μg/m^3) between LCS and BAM-1020 according to concentration ranges measured by LCS.

Parameter	N	Paired differences (BAM-LCS) Mean ± SD	*t* value	Correlation coefficient (*r*)
Total	332	-9.35 ± 18.87	-9.03**	0.63**
LCS ≤ 25 μg/m^3 (Low level)	103	1.03 ± 5.80	1.81	0.67**
25 μg/m^3 < LCS < 50 μg/m^3 (Intermediate level)	158	-7.35 ± 11.33	-8.16**	0.23**
LCS ≥ 50 μg/m^3 (High level)	71	-28.86 ± 28.15	-8.64**	0.23*

* $p < 0.05$, ** $p < 0.01$

3-1. Method of $PM_{2.5}$ spatial variability in Seoul

3-1.1 Sampling sites

To improve the characterization of spatial contrast of $PM_{2.5}$, 20 sampling sites were newly selected supplementary to the regulatory monitoring network in Seoul, Korea (Min et al., submitted). Through k-means clustering, people's residences derived from children' homes of the Atopy Free School survey were categorized based on geographic variables most related to $PM_{2.5}$. Then, regions having relatively poor representative exposure levels were picked and community service centers in those regions were selected for sampling sites.

The city of Seoul is normally divided into the five living quarters considering the topography according to the Han river, the major mountain and the linkage of activity structure by traffic with surrounding metropolitan cities (Kim, 2009). Thus, sampling sites were classified and given IDs are according to their geographical locations into southwest (SW), southeast (SE), central (C), northwest (NW) and northeast (NE) areas of Seoul, Korea. Selected sites including one co-located with regulatory monitoring network (SW4) are described in Table 4 and their location is shown in Fig. 4. Samples were collected at rooftop of community service centers (9~24 meters above ground) on that locations. One site was excluded by nearby construction during monitoring campaign period and also for in map.

Table 4. Summary for 19 sampling sites measured $PM_{2.5}$ in Seoul, Korea.

Site ID	Location	Latitude (°N)	Longitude (°E)	Elevation (m)	Total no. of samples
SW1	Sinwol-1 dong, Yangcheon-gu	37.5327	126.8315	15	11
SW2	Yangpyeong-1 dong, Yeongdeungpo-gu	37.5236	126.8882	12	14
SW3	Singil-6 dong, Yeongdeungpo-gu	37.4994	126.9098	15	12
SW4 (co-located)	Sillim-dong, Gwanak-gu	37.4874	126.9271	15	13
SW5	Bongcheon-dong, Gwanak-gu	37.4881	126.9327	12	14
SW6	Sadang-5 dong, Dongjak-gu	37.4856	126.9669	12	14
SW7	Namhyeon-dong, Gwanak-gu	37.4745	126.9778	18	14
SE1	Bangbae-2 dong, Seocho-gu	37.4797	126.9855	15	12
SE2	Daechi-2 dong, Gangnam-gu	37.5023	127.0641	15	13
C1	Bogwang-dong, Yongsan-gu	37.5262	127.0001	18	14
C2	Hoehyeon-dong, Jung-gu	37.5572	126.9793	15	13
C3	Changsin-2 dong, Jongno-gu	37.5744	127.0108	15	13
C4	Sungin-2 dong, Jongno-gu	37.5748	127.0199	18	12
C5	Pyeongchang-dong, Jongno-gu	37.6062	126.9681	15	14
NW1	Bukgajwa-2 dong, Seodaemun-gu	37.5814	126.9111	12	12
NE1	Anam-dong, Seongbuk-gu	37.5858	127.0213	24	14
NE2	Cheongnyangni-dong, Dongdaemun-gu	37.5862	127.0472	15	14
NE3	Junghwa-2 dong, Jungnang-gu	37.6028	127.0761	9	14
NE4	Muk-2 dong, Jungnang-gu	37.6095	127.0760	12	11

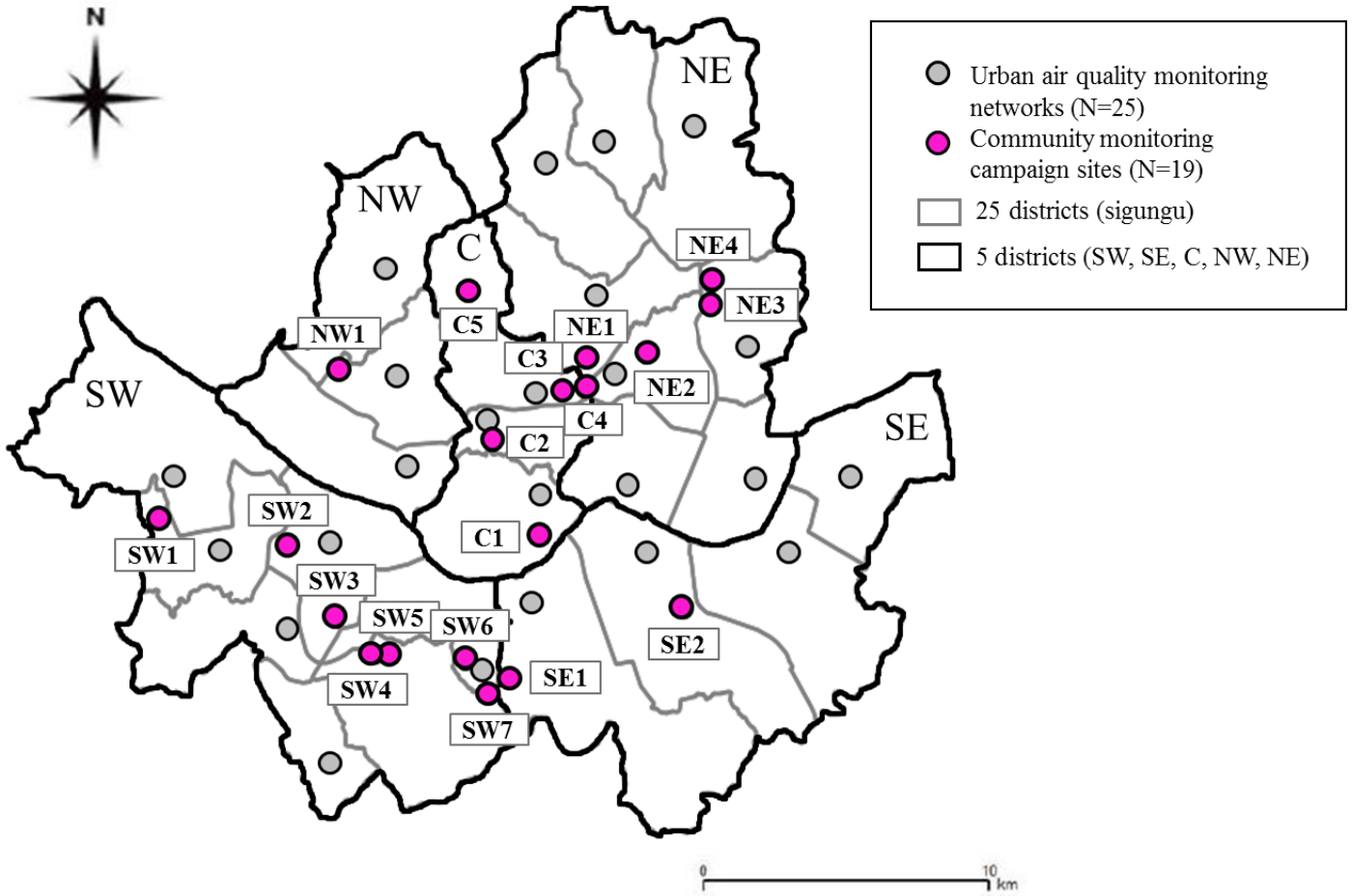

Figure 4. Locations of 19 sampling sites in Seoul, Korea.

3-1.2 Sample collection

Two-week community monitoring campaigns were performed three times for August 2015 to August 2016 in different seasons (between summer and fall, winter and summer). The first monitoring campaign was on August to September in 2015, the second campaign was on February in 2016 and the third was on July to August in 2016. Each campaign was conducted during two-week period. Integrated 24-hour samples were concurrently collected at the 19 sampling sites every 2 to 4 days. All samples were collected using DPIS, operating at 10 L/min, loaded with 47 mm quartz microfiber filters (Whatman, UK) which was pre-baked at 450 ˚C for 12-hour to lower their carbon blanks for the purpose of chemical analyses. Fig. 5 shows the installation of DPIS at one community service center for collecting $PM_{2.5}$.

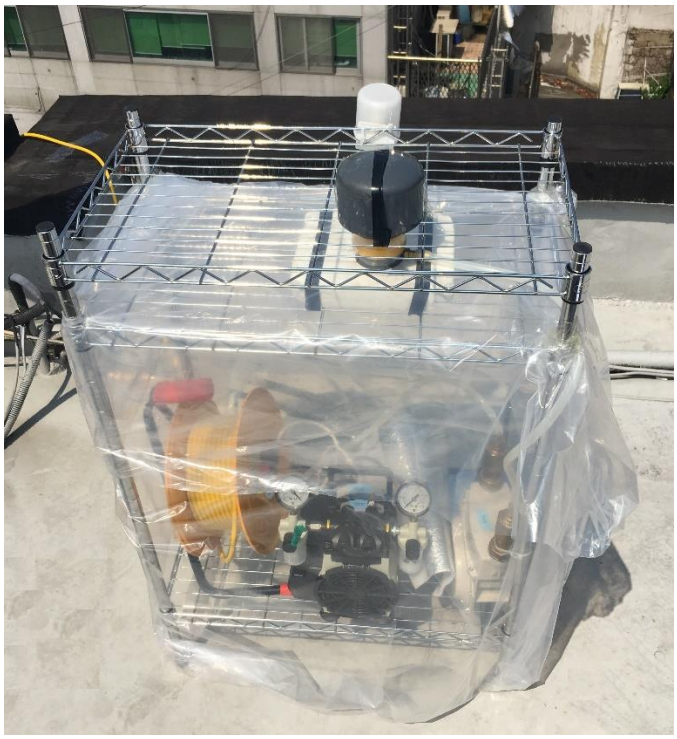

Figure 5. The installation of DPIS at one sampling site.

3-1.3 Sample analysis

Mass concentration of $PM_{2.5}$ samples was determined by measuring the weight of quartz filters before and after collection using a microbalance (Sartorius, Japan, Precision: 0.01 mg) and then calculate the weight differences of them. Collected filters were dried in desiccator at least for 24 hours. Each of filters was weighed three times and the average value of them was used when the difference between the max and min values of three consecutive measurements is less than 0.02 mg.

Organic carbon (OC) and elemental carbon (EC) were analyzed by the National Institute of Occupational Safety and Health (NIOSH) 5040 method with Thermal/Optical Transmittance (TOT) using OC/EC analyzer (Sunset Laboratory Inc., USA). The protocol used in this study about temperature and ramp time of each stage is shown in Table 5. Each quartz filter was punched with standard area of 1.5 cm × 1.0 cm for analysis. OC and EC are measured by quantifying CH_4 which is formed while heating a sample to 870 ˚C in phases. OC concentration is calculated by sum of OC1, OC2, OC3, OC4 and pyrolyzed OC (OC_{pryrol}) and sum of EC1, EC2, EC3, EC4, EC5, EC6 minus OC_{pryrol} is for EC concentration.

After carbon analysis was finished, the ionic species of the filters were analyzed by ion chromatography (IC) which has ion exchange mechanisms using ICS-1100 (Thermo Fisher Scientific Inc., USA). The operating conditions of IC are shown in Table 6. Before IC analysis, samples were extracted into 30 mL deionized water (DIW) with sonication during 4 hours at 60 ˚C and then filtrated using a 0.2 μm syringe filter after rinsing of 2 mL DIW. Nitrate (NO_3^-), sulfate (SO_4^{2-}) and ammonium (NH_4^+) which are dominant ionic components in $PM_{2.5}$ were quantified. Their concentration was calculated by correcting the punched area of the filters to obtain concentration of total exposed area of them.

Table 5. OC and EC operation program for carbon analysis used in this study.

Step	Carrier Gas	Ramp Time (s)	Temperature (℃)
OC1	He	80	310
OC2	He	60	475
OC3	He	60	650
OC4	He	90	870
	He	oven heaters are turned off to cool oven	
EC1	2% O_2 in He	45	550
EC2	2% O_2 in He	45	625
EC3	2% O_2 in He	45	700
EC4	2% O_2 in He	45	775
EC5	2% O_2 in He	45	850
EC6	2% O_2 in He	120	870
	Cal gas + He/O_2	External Std. Calibration and cool-down	

Table 6. Operating conditions of Ion Chromatography for ionic analysis.

Species	Anion (NO_3^-, SO_4^{2-})	Cation (NH_4^+)
Instrument	ICS-1100 (Dionex)	
Column	IonPac AS14 (4 × 250 mm) # 046124	IonPac CS12A (4 × 250 mm) # 046073
Eluent	3.5 mM Sodium Carbonate + 1.0 mM Sodium Bicarbonate	20 mM Methane Sulfonic Acid
Flow rate	1.2 mL/min	1.0 mL/min
Suppressor	AERS 500 4mm # 082540	SC-CSRS 300 4mm # 067530
Standard solution	Seven Anion Standard II # 057590 (Dionex)	Six Cation Standard II # 046070 (Dionex)

3-1.4 Quality assurance and quality control (QA/QC)

All sampling preparations were done in clean room with controlled temperature and relative humidity conditions (20 ± 2 ˚C, 40 ± 5%) and filters were transported with sealed. Impactors provided a particle size cutoff based on the flow rate, so the flow rate was modified within 5% range of 10 L/min before every sampling. The sample was excluded when it's flow rate was out of 10% range. A static eliminator was used before weighing the quartz filters to reduce the errors caused by static. In addition, a blank filter was stored and weighed together with sample filters to be modified any effect of storage and weighing environment. Field blanks were remained on 5 sites of the 19 sites during two weeks every monitoring campaign period. The average concentrations of field and laboratory blank filters were subtracted from sample filter concentrations of each component of $PM_{2.5}$.

In case of carbon analysis, recovery efficiencies were checked before start that they are within 5% range using carbon standard solution including 0.71 g of sucrose in 100 mL flask with DIW. A reproducibility was also checked that it is within 10% by repeating analysis of one sample and relative percent difference (RPD) was calculated using these values. For ion analysis, recovery efficiencies were determined every 20 samples by spiking standard solution of 1.0 ppm of target ions and reproducibility was determined every 10 samples. Their allowable error ranges are same as for carbon analysis. The method detection limit (MDL) of OC and EC was calculated by 3 times standard deviation of field blank concentrations. MDLs of ion species were calculated by multiplying standard deviation of seven spiking 1.0 ppm values and its degree of freedom. The uncertainty of them was computed using these spiking values and standard deviation of field blank values. The uncertainty of OC was reported by the instrument while the calculation of EC uncertainty was followed form of Wisconsin State Laboratory of Hygiene (WSLH) to show better estimation (Dutton et al., 2009). The RPD, MDL and uncertainty of each component are presented in Table 7. There were no any values below MDL in all analytes.

Table 7. Average relative percent difference (RPD), method detection limit (MDL) and uncertainty (Unc.) for each $PM_{2.5}$ component analysis.

	OC	EC	NO_3^-	SO_4^{2-}	NH_4^+
RPD (%)	2.8	5.4	1.7	0.7	0.8
MDL (μg/m^3)	0.8	0.1	0.2	0.2	0.1
Unc. (μg/m^3)	0.6	0.2	0.1	0.1	0.2

3-1.5 Data analysis

3-1.5.1 Spatial distribution

The spatial distribution of $PM_{2.5}$ and its components was represented to show spatial characteristics of arithmetic mean concentrations across days on each site of them. The data were grouped according to season, summer-fall (August-September), winter (February) and summer (July-August). Only days with at least 15 sites that have valid 24-hour concentration measurements were included in the analysis. Due to a limited number of measurements, missing values were substituted to the average across all available sites on each date for better representative values of each site only in case of analyzing spatial distribution.

Also, the relationships between concentrations of $PM_{2.5}$ components at each sampling sites were analyzed for investigating composition characteristics of $PM_{2.5}$. They were expressed as the Pearson correlation coefficient (r) determined using SPSS statistical software (version 22.0, IBM Corp., USA).

3-1.5.2 Spatial variability

The spatial variability of $PM_{2.5}$ mass concentrations and its components were determined using coefficient of spatial variation (CV) and coefficient of divergence (COD). CV and COD provide information on the degree of heterogeneity between sites, which is necessary to determine the number and location of monitoring networks required to obtain reasonable personal exposure level of $PM_{2.5}$ especially in metropolitan areas (Kim et al., 2016; Daher et al., 2013; Bell et al., 2011; Cyrys et al., 2008; Krudysz et al., 2008; Kim et al, 2005). CV is determined as the standard

deviation (SD) of all sampling sites measurements divided by the average of them. CV at each sampling date is defined as follows:

$$\mathrm{CV}_i = \frac{\sqrt{\frac{1}{n}\sum_{j=1}^{n}\left(x_{ij}-\bar{x}_i\right)^2}}{\bar{x}_i} \tag{3}$$

where x_{ij} is the concentration measured at jth site on i^{th} day, $\bar{x}_i$ is the average concentration across the sampling sites on i^{th} day and n is the number of sampling sites. CV implies the extent of dispersion compare to average for measurements across sampling sites on a given day in Seoul. Seasonal CV was calculated as the average of CV in different seasons. CV was exhibited as bar graphs corresponding to one average CV for each components depending on the season. Additionally, CV could also be calculated as other ways different from equation (3). Considering temporal variation, CV could be derived from the average of total sampled values in each sites. In this case, only one CV value in each component is obtained and these CV values could be represented as consistent indicator when it comes to more collected measurements.

COD for each $PM_{2.5}$ mass and its components is calculated the variability of all monitoring site pairs and its equation for a given site pairs is defined as follows:

$$\mathrm{COD}_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}}\right)^2} \tag{4}$$

where X_{ij} and X_{ik} are the concentration on i^{th} day measured at sites j and k and p is the number of sampling days. COD indicate the degree of heterogeniety between all sites' pairs in Seoul. The CV and COD can vary from 0 to 1, with a value of 0 indicating that measurements of $PM_{2.5}$ have no variability within sampling area, whereas the greater values of them implying the higher spatial variability of measurements. COD was presented as boxplots containing all values for site pairs of each components depending on the season.

3-2. Results and discussion of spatial variability in Seoul

3-2.1 Spatial distribution

In the following sections, all reported concentrations correspond to arithmetic averages with seasons distinguished into summer-fall (August-September), winter (February), summer (August) and total sampling period. Respective errors in figures represent standard errors, whereas all in tables represent standard deviation with mean concentrations. All 19 sampling sites presented in figures and tables were arranged from southwest to northeast through the central area of Seoul in the following order: SW, SE, C, NW and NE.

3-2.1.1 $PM_{2.5}$ mass and proportion of chemical components

The seasonal average mass concentration of $PM_{2.5}$ at each of the sampling sites were presented in Table 8. The mass concentration levels of $PM_{2.5}$ have a wide range from 25.4 to 46.1 μg/m^3 across the seasons and sites. The greatest mass concentration was in winter, whereas the lowest in summer. This is because the usage of energy is increased in winter and moreover relatively lower mixing height disturbed to dispersion of air pollutants than summer which has a frequent precipitation in Seoul, Korea (Kim and Kim, 2008). The mass concentration in wintertime was greatest at SW4 and lowest at SW6 in wintertime (46.1 ± 12.7 and 36.5 ± 7.9 μg/m^3, respectively). On the other hand, the concentrations in summer were highest at SW1 and lowest at SE1 (25.4 ± 8.0 and 33.1 ± 7.0 μg/m^3, respectively). In overall, SW6 and SE1 sites appear the low mass concentrations during sampling period. Two sites have a common location of right nearby urban park with green spaces. These urban neighborhood parks have

almost no sources of emissions and they promote the smooth flow of airflow, which have highly effect in suppressing deterioration of air pollution (Ju et al., 2005). Thus, two sites of low mass concentration would have been affected by air pollution reduction effect of urban parks.

Spatially, the four sites in the edge of southwest area (SW1 ~ SW4) and two sites in central area (C1, C2) were shown relatively high mass concentrations more than average concentrations on each seasonal basis (summer-fall: 34.5, winter: 41.2, and summer: 31.0 μg/m^3). The high mass concentration of SW1 to SW4 could be attributed to an industrial complex located in southwest area of Seoul almost 3 ~ 5 km away from those sites. Especially high mass concentrations in winter at SW1 to SW4 above 40 μg/m^3 were may due to increase of heating fuel usage in industrial complex with reduced mixing height during the winter. Also, the major traffic-induced sites designated by Seoul city government were located in *Yeongdeungpo*-gu, *Yongsan*-gu and *Jung*-gu, and SW2, SW3, C1 and C2 are also located in those districts. Traffic is one of the major contributor of $PM_{2.5}$ in metropolitan city such as Seoul. Therefore, the cause of high mass concentrations could be accounted as high volume of traffic in southwest and central area of Seoul.

The mass concentration of $PM_{2.5}$ and its chemical components concentration at each sampling sites during summer-fall, winter and summer are shown in Fig. 6. The chemical species of $PM_{2.5}$ were analyzed for OC, EC and ionic species including nitrate, sulfate and ammonium. On an average basis of total sampling period, the chemical composition of $PM_{2.5}$ consisted of 18-22% OC, 3-4.1% EC, 8-9.5% nitrate, 17.5-20.6% sulfate and 9-10% ammonium of total mass, as shown in Table 9. These percent fractions are within the ranges with previously reported study of Kim and Kim (2008) except for slightly high proportion of nitrate to sulfate in this study. The studies of Kim et al. (2007) and Heo et al. (2009) are reported larger proportion of EC to total mass than this study. As can be inferred, OC is the major components of $PM_{2.5}$ slightly after sulfate. Secondary ion constituents were also dominant, contributing to almost 40% of $PM_{2.5}$ mass. The total fraction of components was less than 50% only in 1st period in summer-fall season. It could

be accounted for relatively heavy precipitation (over 20 mm) during that period, which could affect to lower water-soluble components of $PM_{2.5}$.

As shown in Table 9, the average percent fraction of $PM_{2.5}$ was varied across the sites especially in EC and nitrate. EC is considered as a tracer for diesel engine emissions and nitrate is highly associated with NO_X emissions particularly from automobiles in urban area (Hand et al., 2012; Schauer et al., 2003). In other words, it indicates that EC and nitrate are transportation factors contributed to $PM_{2.5}$. $PM_{2.5}$ measurements at SW6 showed highest proportion of nitrate on the basis of total period average (9.5 ± 9.9%), despite of generally low mass concentrations under average concentrations of overall sampling sites. The average proportion of EC to $PM_{2.5}$ was highest at NE4 (4.1 ± 1.5%). Both SW6 and NE4 were commonly located nearby subway station away from 1.5 to 3.0 m. Thus, high proportion of EC and nitrate in $PM_{2.5}$ could be affected by the site location, though it does not directly correlate with absolute concentrations. The detail of components and their ratios were illustrated in following sections.

Table 8. Seasonal mass concentration (average ± standard deviation) of $PM_{2.5}$ at 19 sampling sites.

	Summer-Fall (N=4)	Winter (N=4)	Summer (N=6)	Total period (N=14)
SW1	40.7 ± 9.0	44.5 ± 13.1	33.1 ± 7.0	38.5 ± 10.1
SW2	37.1 ± 9.9	42.9 ± 12.8	32.8 ± 7.2	36.9 ± 9.9
SW3	39.8 ± 6.2	42.2 ± 12.9	31.9 ± 7.2	37.1 ± 9.5
SW4	37.8 ± 4.9	46.1 ± 12.7	31.8 ± 6.6	37.6 ± 9.8
SW5	33.3 ± 9.3	41.5 ± 11.1	32.0 ± 9.6	35.1 ± 10.1
SW6	26.1 ± 1.1	36.5 ± 7.9	29.5 ± 7.1	30.5 ± 7.2
SW7	32.8 ± 9.7	39.1 ± 9.9	32.5 ± 7.8	34.5 ± 8.8
SE1	31.5 ± 5.5	40.9 ± 9.0	25.4 ± 8.0	31.5 ± 9.7
SE2	37.3 ± 9.3	39.5 ± 8.5	30.3 ± 7.2	35.0 ± 8.6
C1	38.2 ± 4.3	42.5 ± 12.0	31.1 ± 8.1	36.4 ± 9.4
C2	39.0 ± 8.4	41.5 ± 9.9	31.0 ± 7.8	36.3 ± 9.3
C3	36.4 ± 10.7	44.1 ± 8.3	30.8 ± 8.8	36.2 ± 10.2
C4	37.0 ± 11.0	41.6 ± 8.2	31.6 ± 6.9	36.0 ± 9.0
C5	32.8 ± 8.0	41.0 ± 13.0	29.9 ± 8.3	33.9 ± 10.2
NW1	36.1 ± 5.5	41.1 ± 12.5	31.8 ± 7.0	35.7 ± 8.8
NE1	35.1 ± 11.4	36.9 ± 8.5	28.9 ± 7.4	32.9 ± 9.0
NE2	28.8 ± 10.7	38.9 ± 11.2	32.0 ± 8.7	33.0 ± 10.0
NE3	27.8 ± 10.0	40.2 ± 8.1	31.3 ± 7.4	32.9 ± 9.2
NE4	27.9 ± 12.2	41.7 ± 8.9	31.9 ± 8.1	33.6 ± 10.5

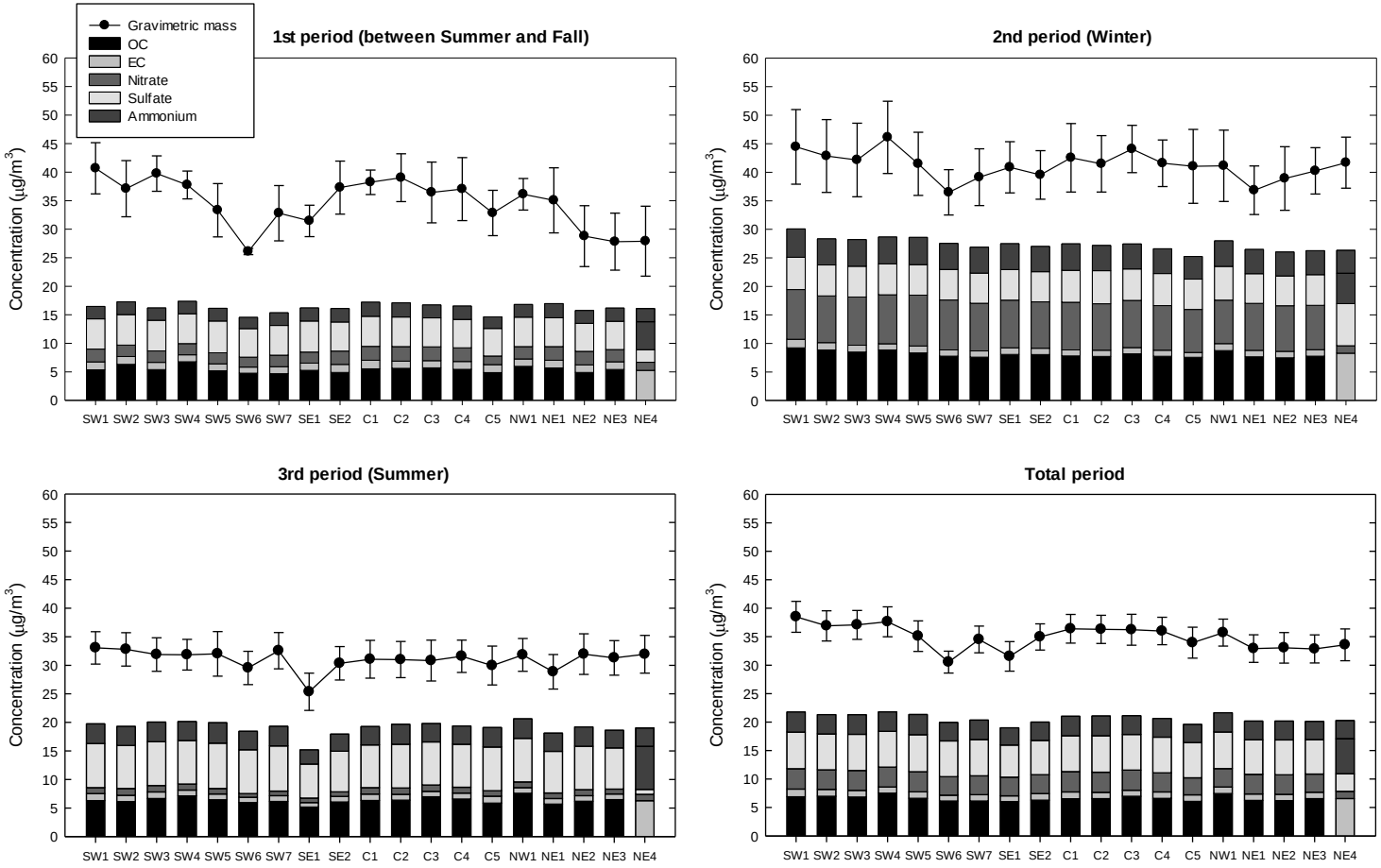

Figure 6. Chemical composition and gravimetric concentration of $PM_{2.5}$ by site in summer-fall, winter, summer and total period. Error bars correspond to one standard error.

Table 9. Average (± standard deviation) percent fraction of $PM_{2.5}$ components at the 19 sampling sites during total period.

	OC	EC	NO_3^-	SO_4^{2-}	NH_4^+
SW1	18.1 ± 4.7	3.6 ± 1.1	8.3 ± 8.0	17.6 ± 7.5	9.4 ± 3.9
SW2	19.3 ± 4.7	3.4 ± 0.9	8.3 ± 7.5	18.1 ± 7.7	9.1 ± 3.7
SW3	19.2 ± 5.5	3.4 ± 0.9	8.4 ± 8.1	17.8 ± 7.3	9.1 ± 4.0
SW4	20.6 ± 4.8	3.0 ± 0.8	8.0 ± 7.3	17.5 ± 7.7	8.9 ± 3.8
SW5	19.4 ± 4.7	3.4 ± 0.9	8.9 ± 8.7	19.6 ± 8.4	10.0 ± 4.0
SW6	20.3 ± 3.8	3.5 ± 1.2	9.5 ± 9.9	20.6 ± 7.2	10.0 ± 3.8
SW7	18.3 ± 5.1	3.4 ± 1.3	8.6 ± 8.6	18.7 ± 6.8	9.4 ± 3.4
SE1	19.8 ± 4.5	3.5 ± 1.4	8.5 ± 8.1	18.8 ± 7.2	9.1 ± 3.7
SE2	18.4 ± 4.8	3.4 ± 1.3	8.3 ± 8.2	17.8 ± 7.6	8.9 ± 3.7
C1	18.6 ± 4.8	3.5 ± 1.5	8.7 ± 8.1	18.1 ± 7.7	9.1 ± 4.2
C2	18.8 ± 5.4	3.2 ± 0.9	8.6 ± 7.9	18.3 ± 7.6	9.4 ± 3.8
C3	19.9 ± 4.8	3.1 ± 0.9	8.4 ± 7.3	18.5 ± 9.2	8.9 ± 4.0
C4	18.8 ± 4.4	3.2 ± 1.0	8.4 ± 8.0	18.2 ± 7.7	9.0 ± 4.0
C5	18.6 ± 5.1	3.8 ± 1.6	7.8 ± 7.3	19.1 ± 7.8	9.4 ± 3.5
NW1	21.7 ± 6.4	3.3 ± 0.9	8.0 ± 7.2	18.8 ± 8.2	9.4 ± 3.8
NE1	19.6 ± 4.7	3.5 ± 1.1	9.4 ± 9.0	19.1 ± 7.5	9.8 ± 3.5
NE2	19.6 ± 5.2	3.7 ± 1.8	9.3 ± 8.0	19.7 ± 9.6	9.9 ± 4.2
NE3	20.5 ± 4.7	3.6 ± 1.3	8.4 ± 7.6	19.4 ± 9.8	9.5 ± 3.8
NE4	20.4 ± 4.8	4.1 ± 1.5	8.1 ± 6.7	20.2 ± 11.7	9.8 ± 4.6

3-2.1.2 Carbonaceous species

EC is emitted directly into the atmosphere and is considered as a key marker of diesel emission especially in urban areas (Schauer, 2003). Nevertheless, it is a minority component of $PM_{2.5}$, accounting for 2.3-5.5% of its total mass ranging from 0.8 to 1.5 μg/m^3 across the seasons and sites, as shown in Fig 6 and its percent fraction on a total average basis shown in Table 9. The lowest level of EC was shown at different sites depending on season. SW6, C5 and SE1 sites have lowest level of EC in summer-fall, winter and summer respectively. The site of SW6 and SE1 could have a low concentration of pollutants because of their location nearby urban park, as described earlier. C5 site is located at the uppermost in central area, which is 3.6 km away from a congested main road in central area. On the contrary, the large concentration of EC generally occurred at SW1 during total sampling period (1.35 ± 0.38 μg/m^3) due to its adjacent to a highway interchange (away from 0.8 km). Consequently, the highest EC concentrations were observed at SW1 across the sites during winter (1.50 ± 0.34 μg/m^3) and summer (1.24 ± 0.29 μg/m^3) except for summer-fall period. The overall EC concentrations in summer-fall period were generally higher than other period and in contrast OC concentrations were generally lower than others. The low OC concentrations could be explained as the heavy rain during that period with washing away a portion of water-soluble OC (WSOC) component. Contrary to OC, EC is known to be hydrophobic although it could acquire hydrophilic characteristics through chemical aging (Zhao et al., 2016). Thus, the high concentrations of EC in summer-fall season could be illustrated that there were dominant emissions from local primary sources during the period on the assumption that EC concentrations were not affected by precipitation.

Unlike EC, OC can be directly emitted from fossil fuel combustion, known as primary OC (POC), or derived from photo-oxidation process in the atmosphere, known as secondary OC (SOC) (Turpin et al., 1991). OC was major component in $PM_{2.5}$ across the site and season, accounting for 13-24% of its total mass ranging from 4.7 to 9.2 μg/m^3. Although the uncertainty of OC values

by underestimating WSOC components in summer-fall period, the data could be valuable because vehicle emissions are mostly contained water insoluble organic carbon (WISOC), not WSOC (Weber et al., 2007; Ruellan and Cachier, 2001; Tobias et al., 2001). As shown in Fig. 7, peak concentrations of OC with over the average repetitively occurred at SW4 and NW1 in summer-fall (6.79 ± 1.17 μg/m^3 and 5.98 ± 1.37 μg/m^3, respectively), winter (8.86 ± 1.54 μg/m^3 and 8.75 ± 0.96 μg/m^3, respectively) and summer (7.13 ± 1.82 μg/m^3 and 7.58 ± 1.71 μg/m^3, respectively). It was likely due to the nearby emission sources of their locations that a resource recovery facility is in location about 3 km away from NW1, and SW4 is located in specialized street of restaurants with many of using charcoal fire. OC measurements were showed higher concentration in winter than summer at all locations, which could be explained as condensing due to low mixing height in winter.

To estimate the extent of POC and SOC contribution to total OC, the variation of OC/EC ratio according to season as described in Table 10 at each of the sites. The OC/EC ratios were generally higher in winter compared to summer except for NW1 site which has distinct high concentration of OC in summer. However, with the exception of summer-fall period, the OC/EC ratios in this study were greater than previous reported values of studies in Seoul (2.8 ~ 4.7), which were likely due to the low level of EC relative to OC in overall season (Ham et al., 2017; Lee et al., 2015c; Kim et al., 2010; Kim et al., 2007). It has been reported that SOC possibly affect to OC formation when the ratio of OC/EC is over 2.5 or 2.0 (Turpin and Huntzicker 1995; Chow et al., 1996), but it could be different according to regions. Also, the Pearson correlation coefficients between OC and EC were 0.81, 0.77 and 0.34 in summer-fall, winter and summer, respectively. Although considering the high correlation in summer-fall was derived from missing part of WSOC components, there were obvious seasonality in correlation between OC and EC. Consequently, it can be inferred that the primary emission sources were abundant particularly in winter relative to summer which was not thoroughly explained OC by POC or EC emissions due to increased photochemical reaction in summer.

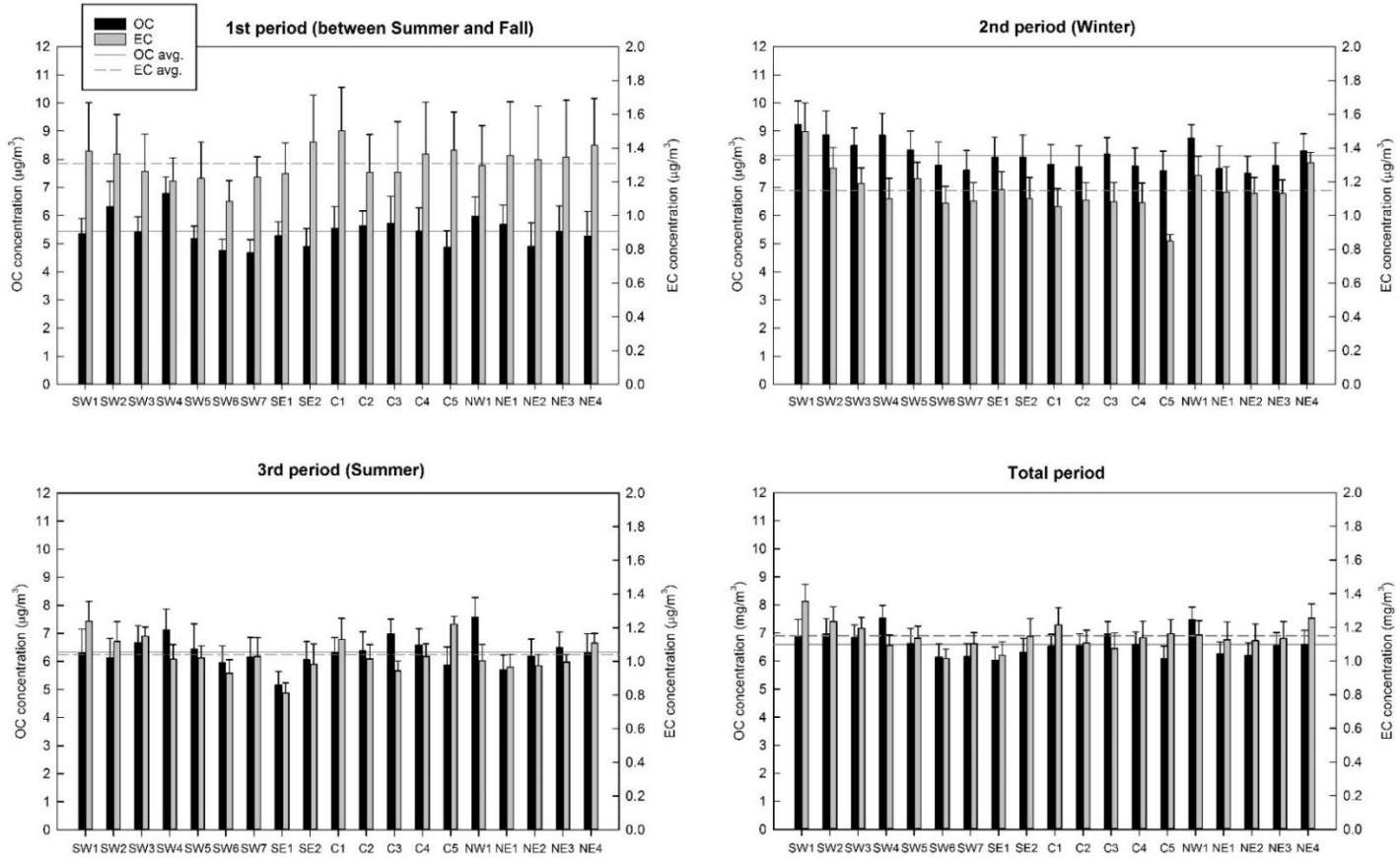

Figure 7. Average concentration of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ by site in summer-fall, winter, summer and total period. Error bars correspond to one standard error.

Table 10. Average ratio (± standard deviation) of organic carbon (OC) to elemental carbon (EC) at the 19 sampling sites.

	Summer-Fall (N=4)	Winter (N=4)	Summer (N=6)	Total period (N=14)
SW1	4.2 ± 1.0	6.2 ± 0.3	5.2 ± 1.7	5.2 ± 1.4
SW2	4.8 ± 1.3	6.9 ± 0.4	5.6 ± 1.0	5.7 ± 1.2
SW3	4.4 ± 0.7	7.2 ± 0.3	5.8 ± 1.2	5.8 ± 1.3
SW4	5.7 ± 0.6	8.2 ± 0.9	7.0 ± 0.9	7.0 ± 1.2
SW5	4.5 ± 0.8	6.9 ± 0.6	6.3 ± 1.4	5.9 ± 1.4
SW6	4.5 ± 0.6	7.2 ± 0.9	6.6 ± 1.5	6.2 ± 1.6
SW7	3.8 ± 0.1	7.1 ± 0.6	6.1 ± 1.4	5.7 ± 1.6
SE1	4.4 ± 0.6	7.0 ± 0.2	6.4 ± 1.3	6.0 ± 1.4
SE2	3.5 ± 0.4	7.4 ± 0.8	6.4 ± 1.6	5.9 ± 1.9
C1	3.7 ± 0.2	7.5 ± 0.8	5.8 ± 1.4	5.7 ± 1.7
C2	4.8 ± 1.2	7.1 ± 0.5	6.4 ± 1.4	6.1 ± 1.4
C3	4.8 ± 0.7	7.7 ± 0.7	7.5 ± 1.4	6.8 ± 1.7
C4	4.2 ± 0.6	7.3 ± 0.8	6.5 ± 1.5	6.1 ± 1.6
C5	3.6 ± 0.4	9.0 ± 1.8	4.8 ± 1.2	5.7 ± 2.5
NW1	4.8 ± 0.9	7.1 ± 0.6	7.6 ± 0.8	6.7 ± 1.5
NE1	4.6 ± 1.1	6.9 ± 1.6	6.1 ± 1.5	5.9 ± 1.6
NE2	3.9 ± 0.6	6.7 ± 0.8	6.4 ± 1.3	5.7 ± 1.6
NE3	4.3 ± 0.8	6.9 ± 1.0	6.5 ± 1.4	6.0 ± 1.5
NE4	3.8 ± 0.4	6.3 ± 0.7	5.7 ± 1.5	5.3 ± 1.4

3-2.1.3 Ionic species

The seasonal average concentration of ionic species such as nitrate, sulfate and ammonium at each of the sampling sites were shown in Fig. 8. These ions are called as secondary ions (SI) because they are mostly originated from secondary reaction of ammonia with nitric and sulfuric acid in the atmosphere (Hughes et al., 2000). In overall period, sulfate was dominant species among SI, accounting for 11.9-25.4% of $PM_{2.5}$ mass. An overall low level of ionic species concentrations may due to precipitation by carrying away a part of water-soluble ions as same reason of OC, but the data was remained intactly to grasp the spatial tendency of high and low.

The particular thing in the seasonal distribution of SI, the nitrate concentration extremely surged in wintertime displaying a significant seasonal contrast and even accounted for 17.2-23.5% of total mass in winter. Previous study showed that particulate nitrate contributions to total mass of $PM_{2.5}$ could increase according to the increase of $PM_{2.5}$ mass loadings (Yin and Harrison, 2008). Also, high level of nitrate in winter can be explained as the result of the reaction between gas-phase ammonia and nitric acid to form particulate-phase ammonium nitrate favored by the low ambient temperature (Kaneyasu et al., 1995), and the additional NO_x emission from domestic heating leading to high availability of precursor NO_x required to form particulate nitrate in winter (Lonati et al., 2005). On the contrary, the concentration of nitrate dropped almost to ~1 μg/m^3 in summertime. This is because the active reaction of dissociation of particulate ammonium nitrate is occurred in high temperature in warm season (Mozurkewich, 1993).

Meanwhile, nitrate concentration showed notable spatial variability across the sampling sites relative to other ionic components especially in summer. Seasonally, the five district area of Seoul showed different patterns about high and low concentration of nitrate. In summer-fall season, high level of nitrate was concentrated in central area (2.3-2.6 μg/m^3) above the average value of 2.1 μg/m^3, except for C5 site (1.5 μg/m^3). It has similar pattern in summer period that all central area except for C5 was over and the average (1.0-1.1 μg/m^3) addition to the high concentration in

five site in SW area, SW1 to SW5 (~1.2 μg/m^3). Whereas for the winter season, there was no obvious domination in central area of high concentration but concentrated in all of SW area (8.2-8.9 μg/m^3). SW6 and C5 which had low mass and EC concentration by their condition of location also commonly presented generally low levels of nitrate except for SW6 site in winter season (8.8 μg/m^3). Collectively, this trend implies that a transport was the major contributor of particulate nitrate in central and southwest area, and in case of winter, industrial heating was mainly contributed to nitrate concentration in sites of SW area located nearby industrial complex.

Sulfate which is a dominant component of SI mostly emitted from fossil fuel combustion had poor spatial variability across the season, but slightly increase in variability and concentration in winter according to increase of domestic heating. In summer, the sulfate concentration notably increased and even accounted for 22.2-25.4% of total $PM_{2.5}$ mass concentration. These summertime peaks in sulfate concentrations are mainly due to higher SO_2 oxidation rates facilitated in high relative humidity conditions (Tai et al., 2010).

The average of total period ammonium concentration is approximately same as nitrate (3.31 μg/m^3 and 3.37 μg/m^3, respectively) though agricultural land or stock farm are very lacked in Seoul. This is probably due to long-range transport from China and Heo et al. (2009) also reported that large scale of agricultural areas in China could affect to Seoul as large ammonium emission source contrary to secondary nitrate and sulfate mainly emitted from local sources. Particulate ammonium was also likely caused by vehicle-emitted, but Chang et al. (2015) reported that ammonia, as a precursor to particulate ammonium, is not primarily emitted from transportation.

Furthermore, an ion balance was calculated and displayed in Fig. 9 for all sampling sites on basis of seasonal average. Ion balance was performed by determining *J* which means the availability index of ammonium calculated as a ratio of $2[SO_4^{2-}]+[NO_3^-]$ to $[NH_4^+]$ (Chu, 2004). A value of 1 indicates that sulfate and nitrate are fully neutralized by ammonium in the form of ammonium nitrate and ammonium sulfate. Likewise, a value below 1 of *J* suggests that particles

in the atmosphere are partially acidic and otherwise over 1 of *J* implies particles are alkaline. The Pearson coefficient between $2[SO_4^{2-}]+[NO_3^-]$ and $[NH_4^+]$ was 0.97-0.99 on a seasonal basis in this study, indicating that principal formations of nitrate and sulfate in $PM_{2.5}$ were ammonium nitrate and ammonium sulfate. As can be inferred, ammonium was generally present in insufficient amounts to fully neutralize sulfate and nitrate during sampling period in this study with most of *J* values under 1 especially in summer-fall season. The large extent of low level of *J* in summer-fall period could be described by heavy rainfall, which could be strongly affect particulate ammonium to dilute in rain water relative to two other secondary ions (Ouyang et al., 2015). Nevertheless, only a few sites show slightly over 1 value of *J* particularly in winter in SW1 to SW5 (1.02-1.06), but it means almost neutralization by ammonium with the average of reaching almost 1 value of *J* in winter and summer (0.99 ± 0.09 and 1.00 ± 0.14, respectively).

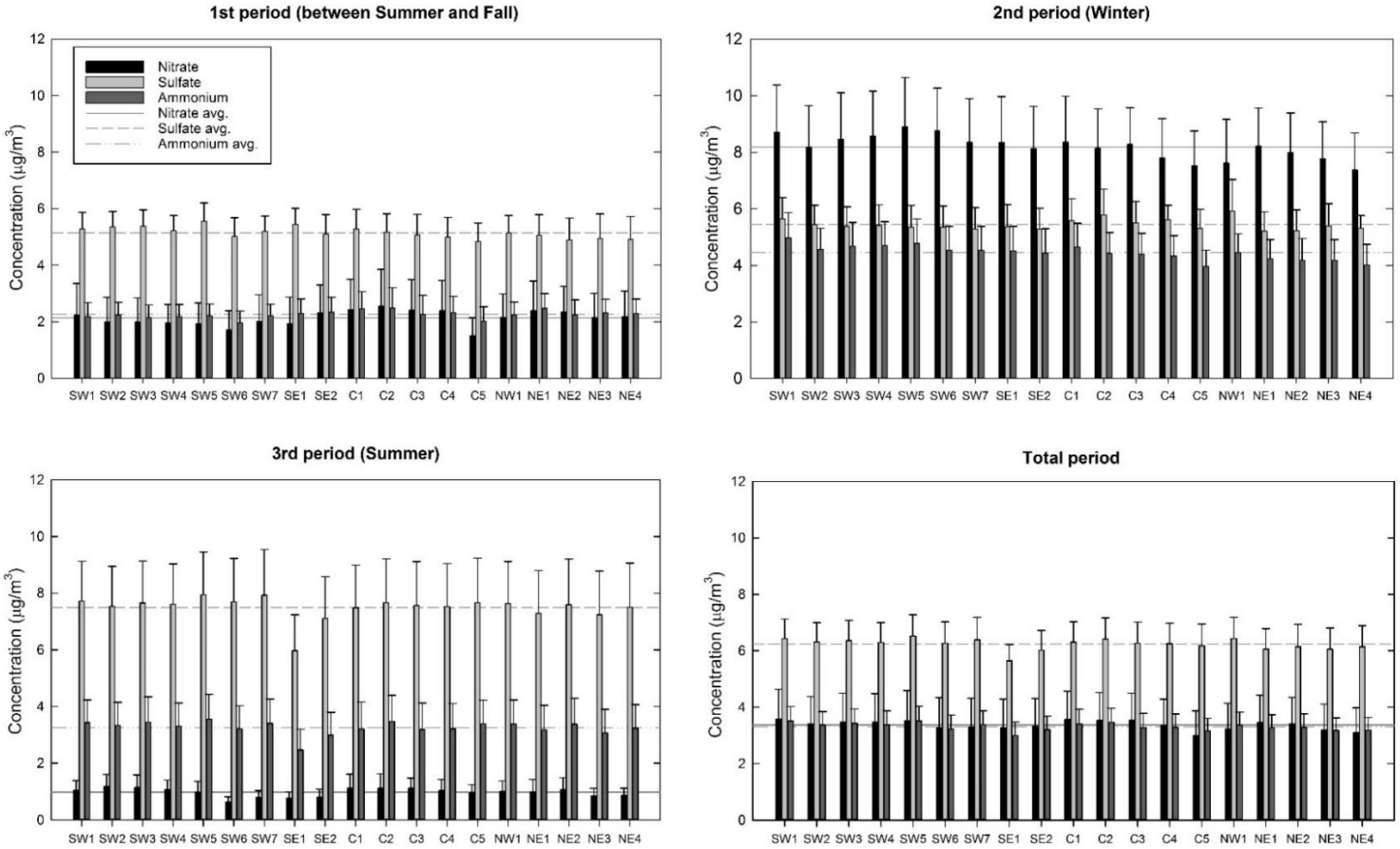

Figure 8. Average concentration of nitrate, sulfate and ammonium in $PM_{2.5}$ by site in summer-fall, winter, summer and total period. Error bars correspond to one standard error.

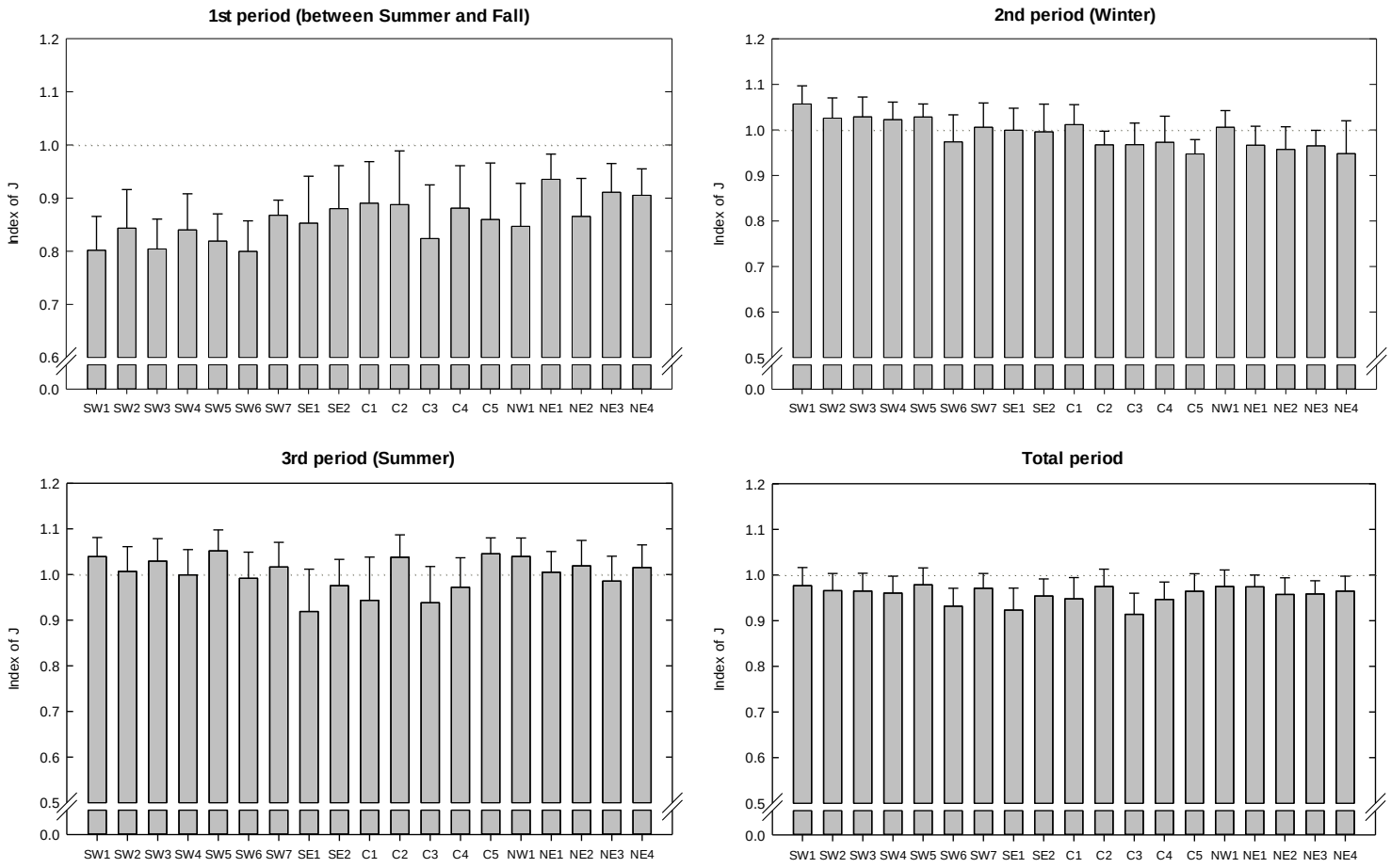

Figure 9. Average value of *J* indicating neutralization by ammonium in summer-fall, winter, summer and total period. Error bars represent one standard error.

3-2.1.4 Correlation between components

The correlation coefficients between components at all sampling sites were exhibited in Table 11. These results indicate relation between components not the causality between them. There were no any statistically significant correlation coefficients between sulfate and others at every sampling sites except for ammonium. Also for ammonium, it didn't correlate with OC at any sites and EC had no correlation with any ionic species across the sites in this study. At every 19 sampling sites, particulate nitrate showed relatively high correlation ($r > 0.5$) range from 0.63 at NE1 to 0.80 at SE1. OC, a major component of $PM_{2.5}$, also show high correlation (0.55-0.80) but some sites were not correlated well. As can be inferred in previous section, particulate ammonium presented generally high correlation with nitrate and sulfate at many of sites (0.70-0.88 and 0.54-0.86, respectively), in agreement with previous studies (Son et al., 2012; Kang et al., 2004). Interestingly, some sites had high correlation between nitrate and OC (0.59-0.86) even there was no any statistically significant correlation between nitrate and ammonium. It could be inferred that some portion of nitrate could be related with organic nitrate, which might represent an important constituent of WSOC (Saxena and Hildemann, 1996), significantly emitted from diesel tailpipe especially at NE4 (Lee et al., 2015b). On this wise, these results could contribute to understand the characteristics of pollutants' resources at each sites despite of limited number of measurements.

Table 11. Significant ($p < 0.01$ or $p < 0.5$) correlation (the Pearson r) between total period average concentrations for different components at each sampling sites. Missing value indicates that correlation was not statistically significant.

	$PM_{2.5}$ mass				OC		NH_4^+	
	OC	EC	NO_3^-	NH_4^+	EC	NO_3^-	NO_3^-	SO_4^{2-}
SW1	0.67	0.69	0.68	-	-	0.72	0.86	-
SW2	0.68	0.60	0.70	0.54	0.55	0.58	0.67	0.71
SW3	-	-	0.66	-	-	0.75	0.63	0.70
SW4	0.59	-	0.78	-	0.59	0.60	0.59	0.77
SW5	0.60	0.54	0.65	0.62	-	0.59	0.64	0.70
SW6	0.73	-	0.69	0.88	-	0.69	0.61	0.71
SW7	-	-	0.66	0.80	-	0.60	0.58	0.73
SE1	0.73	-	0.80	0.81	-	0.78	0.74	0.77
SE2	-	-	0.74	0.68	-	0.84	0.63	0.71
C1	0.57	-	0.71	0.62	-	0.60	0.67	0.76
C2	-	-	0.67	-	-	-	0.60	0.88
C3	0.61	-	0.73	-	-	-	-	0.83
C4	0.68	0.70	0.64	-	-	0.73	-	0.73
C5	0.67	-	0.69	0.54	-	0.67	-	0.83
NW1	-	-	0.77	0.62	0.73	-	0.59	0.74
NE1	0.62	0.60	0.63	0.63	-	0.74	0.60	0.77
NE2	0.55	-	0.66	0.69	-	0.59	0.54	0.81
NE3	0.68	-	0.75	0.78	-	0.63	0.57	0.78
NE4	0.80	-	0.75	0.74	-	0.86	-	0.77

3-2.2 Spatial variability

To determine the spatial variability of $PM_{2.5}$ in Seoul, Korea, CV and COD were calculated for all sampling sites. The CVs were estimated using all 19 sites' values of each date and displayed on a basis of seasonal average, as shown in Fig. 10. In summer-fall, $PM_{2.5}$ mass and nitrate show relatively high levels of CV (both equally 0.21 ± 0.05) and EC in winter (0.15 ± 0.02) and nitrate in summer (0.24 ± 0.04) have peak compared to others. Sulfate presented generally low level of CV during total sampling period (0.07 ± 0.02). For CV values calculated using the average measurements in each sites, as shown in Fig. 11, was generally lower than the preceding values except for nitrate in summer-fall period (0.22). However, despite of decreased values, overall pattern was preserved such as showing winter peak in EC and summer peak in nitrate.

Also for the CODs, as shown in Fig. 12, showed a similar pattern with CVs with a lot of outliers. COD could be represented as the range within region, single-valued maximum (Yi et al., 2016; Ott et al., 2008), average or median (Krudysz et al., 2009; Wilson et al., 2005). Although the spatial variability is determined relatively in comparison with each other, COD values over 0.2 generally indicate heterogeneous between sites (Wilson et al., 2005). The COD of $PM_{2.5}$ mass during total period in this study (0.10 ± 0.03, range of min to max is 0.04-0.19) was lower than reported values of Ghim et al. (2015) in Seoul for $PM_{2.5}$ mass (0.20 ± 0.04, range of 0.10-0.31). Among the component of particulate matter, EC and nitrate normally have high spatial variability in intra-urban scale relative to OC, sulfate and ammonium (Daher et al., 2013). It was agreement with the results of this study that median COD of EC in winter (0.08) and nitrate in summer (0.15) were peak compared to other components. The high level COD of EC and nitrate indicate that traffic emission in the absence of industrial activities mainly cause spatially non-uniform effect in pollutants in metropolitan area. The high level COD of nitrate in summer-fall and summer season may be caused by the increased photochemical reaction of particulate ammonium nitrate segregation, which may occur in spatially different due to topography of each sampling sites.

Although the values of EC and nitrate are below 0.2, it shouldn't be concluded that all components are homogeneous in Seoul because the samples were measured at locations with similar conditions possible to represent residents' exposure level in Seoul rather than sites in right next to roadside or in industrial condensed area. Thus, these results about CV and COD in Seoul for $PM_{2.5}$ suggest that spatial variability in some of $PM_{2.5}$ components on intra-community scale should be considered when investigating the population exposure to $PM_{2.5}$ in Seoul.

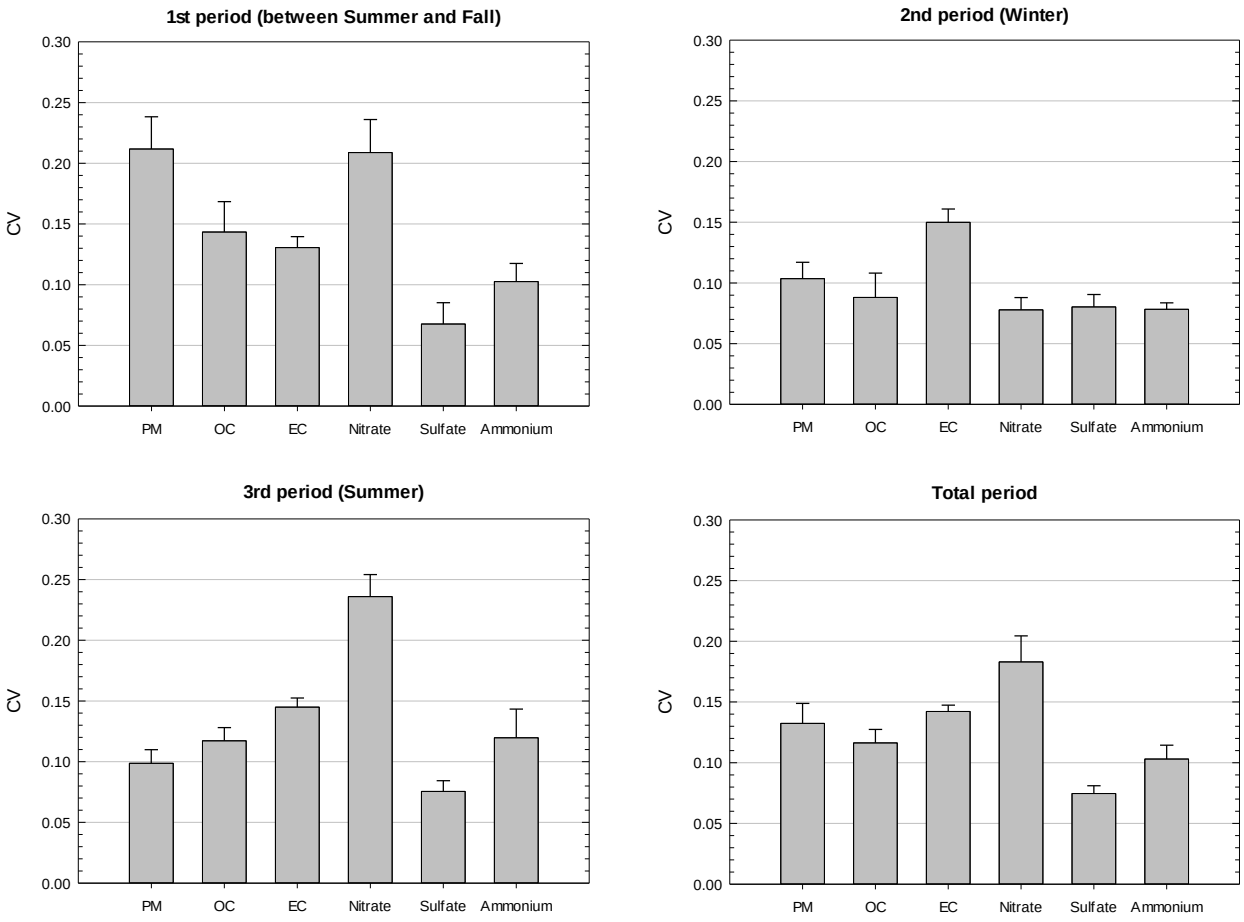

Figure 10. Average value of coefficient of spatial variance (CV) across the 19 sampling sites for each chemical component of $PM_{2.5}$ in summer-fall, winter, summer and total period. Error bars represent one standard error.

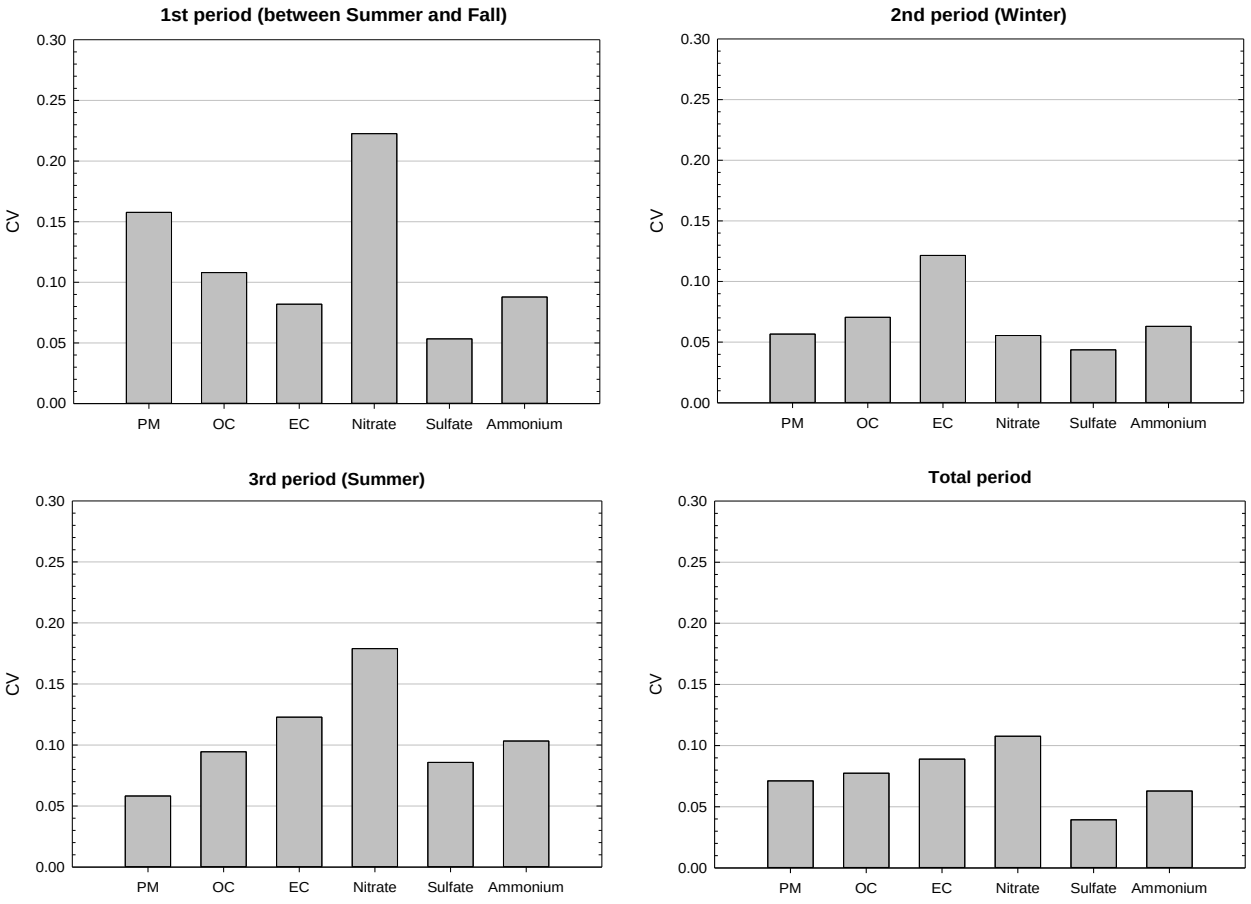

Figure 11. The coefficient of spatial variance (CV) calculated by the average measurement values in each sites for each chemical component of $PM_{2.5}$ in summer-fall, winter, summer and total period.

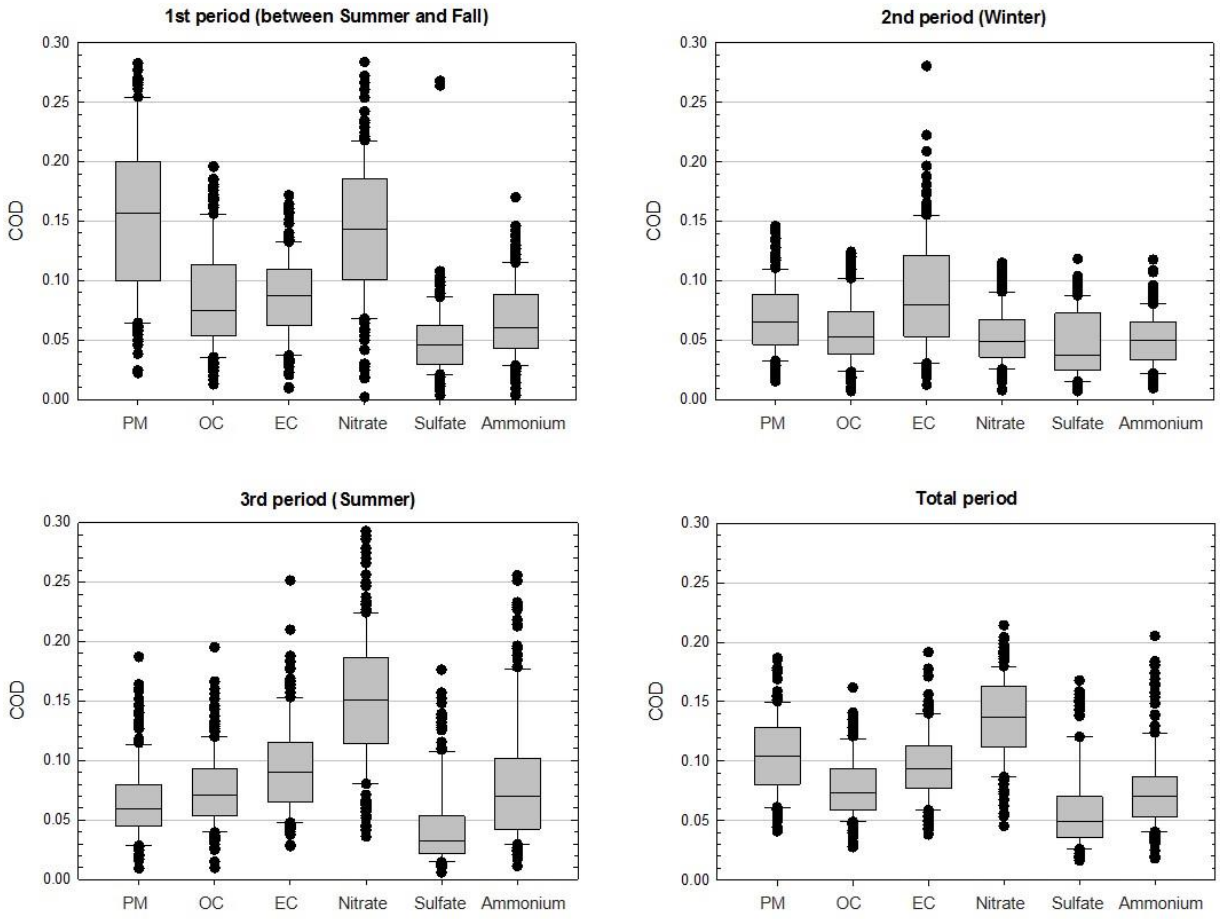

Figure 12. Coefficient of divergence (COD) between site pairs for each chemical component of $PM_{2.5}$ in summer-fall, winter, summer and total period. Box plots show all values including the minimum, first quartile, median, third quartile and maximum.

4. Conclusions

In this study, the spatial and seasonal variability of $PM_{2.5}$ were estimated in order to accurately assess population exposure to $PM_{2.5}$ in complex source emissions, such as megacity of Seoul, Korea. Prior to measure $PM_{2.5}$ in spatial scale, DPIS, cost-effective filter-based sampler, was evaluated its performance for applying spatial sampling and consequently qualified with high reliability and accuracy (97 and 87-89%, respectively). Spatial distribution among the components of $PM_{2.5}$ was varied between sampling sites, especially in EC and nitrate. Likewise, spatial variability was also high in EC and nitrate with computing values of average CV (0.14 and 0.18, respectively) and median COD (0.09 and 0.14, respectively) for total sampling period.

As one part of designing spatial sampling for $PM_{2.5}$, this study suggested the practical applicability of compact sampler, DPIS, to $PM_{2.5}$ spatial monitoring campaign. Simultaneously performed the spatial samplings for $PM_{2.5}$ using DPIS enabled to compare within-urban $PM_{2.5}$ distributions in Seoul. The result of investigating spatial distributions of $PM_{2.5}$ chemical component concentrations showed that the component proportion of $PM_{2.5}$ in Seoul could be mainly attributed to transportation and heating. Furthermore, this study found that EC and nitrate were unevenly distributed relative to other components. It indicates that traffic emission could be a major contributing factor to increase spatial variability of $PM_{2.5}$ in Seoul.

The community monitoring campaign performed in this study was restricted temporally and in number of measurements, so it should be recognized that measurements may could not reflect the representative values at each sites. Also, BAM measurements at regulatory monitoring sites did not consistent with gravimetric method measurements, further comparison sampling between DPIS and BAM is required for combining BAM and DPIS measurements to improve spatial resolution of $PM_{2.5}$ data. In spite of those limitations, this study has significance that spatial $PM_{2.5}$ measurement using filter-based sampler was conducted for the first time in South Korea

and the results in this study could give a practical foundation for intra-urban spatial sampling for $PM_{2.5}$. This study suggests that spatial variability of $PM_{2.5}$ should be considered in the design of epidemiological studies even in intra-urban scale. It is expected that further sampling for combining BAM and DPIS $PM_{2.5}$ data would contribute to better assessment of people's individual exposure to $PM_{2.5}$ in further epidemiological studies.

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국문초록

$PM_{2.5}$ 노출에 대한 사람들의 건강영향은 공간적 변이에 따라 상관성이 있다고 알려져 있다. 그러나, 현재 운용중인 정부 상시측정망은 역학적인 목적으로 구축된 것이 아니기에, 사람들의 거주지에서 대기오염 노출에 대한 영향을 추정하는 데에는 한계가 있을 수 있다. 따라서 이러한 한계를 극복하고, $PM_{2.5}$ 의 공간적 특성에 대한 더 나은 이해를 위하여, 2015 년 8 월부터 2016 년 8 월까지 총 세 차례에 걸쳐 단기간 공간 샘플링을 시행하였다. 각 샘플링은 2 주간 진행되었으며, 서울시 19 개 사이트에서 Deployable Particulate Imapct Sampler (DPIS)를 이용하여 $PM_{2.5}$를 채취하였다.

DPIS 를 이용하여 공간 샘플링을 시행하기에 앞서, DPIS 의 성능 평가를 실시하였다. 성능 평가는 서울대학교 연건캠퍼스에 설치되어 2003 년부터 지속적으로 $PM_{2.5}$를 측정 중인 Low-volume Cyclone Sampler (LCS)와 비교하여 이루어졌다. 먼저 동일한 두 대의 DPIS 를 이용하여 상대정밀도 및 평균제곱오차 기반 R^2 을 구하여 재현성을 판단하였다. 상대정밀도는 두 측정기기의 측정값의 합에 대한 차의 비율을 1 에서 뺀 값으로 구하였다. 정확성은 Teflon 및 quartz 필터를 장착한 DPIS (각각 DPIS_T, DPIS_Q)의 $PM_{2.5}$ 질량농도를 LCS 와 비교하여 구하였다. 정확성은 LCS 의 $PM_{2.5}$ 측정값에 대한 DPIS 와 LCS 측정값의 차의 비를 1 에서 뺀 값으로 구하였으며, 더불어 평균제곱오차 기반 R^2 을 계산하였다. 그 결과, DPIS 는 높은 재현성 (평균 상대정밀도 = 97%, R^2 = 0.98)과 전반적으로 높은 정확성을 보였다 (평균 정확도 = 87-89%, R^2 = 0.91). 측정 방법에 따른 측정값의 차이를 알아보기 위하여 LCS 와 베타선 흡수법을

비교하였으며, 그 결과 통계적으로 유의한 차이를 보였으며 (t 값 = −9.0), 특히 고농도일수록 LCS 가 베타선 흡수법에 비하여 더 많은 $PM_{2.5}$ 를 측정하였다.

DPIS 를 이용하여 공간 샘플링을 시행하여 $PM_{2.5}$ 를 채취한 결과, 평균 $PM_{2.5}$ 질량농도는 전체 샘플링 사이트와 계절에 걸쳐 25.4 ~ 46.1 $\mu g/m^3$ 으로 나타났다. 겨울철 질량농도는 안정적인 대기 상태로 인해 다른 계절에 비해 높게 나타났으며, 특히 서울의 남서지역 및 중심부에 위치한 교통혼잡지역에서 높게 나타났다. 여름철 질량농도는 겨울철에 비해 전반적으로 낮았으며, 특히 서울의 남서 및 남동 지역에 위치한 몇몇 사이트들은 근처에 위치한 근린공원의 영향을 받아 낮게 나타난 것으로 추정된다. 서울시 19 개 사이트의 $PM_{2.5}$ 화학적 성분은 전체 샘플링 기간의 평균값 기준으로 18−22% 유기탄소 (OC), 3−4.1% 원소탄소 (EC), 8−9.5% 질산염, 17.5−20.6% 황산염, 9−10% 암모늄염으로 구성되어 있었다. $PM_{2.5}$ 의 주요 구성성분인 OC 는 겨울철에 농도가 높게 나타났으며, 특히 소각시설이나 숯불 음식점 같은 주변 오염원의 영향을 받아 계절에 상관없이 일관적으로 높게 나타나는 사이트가 존재하였다. 반대로 EC 의 경우에는 일관적으로 높은 농도를 나타내는 사이트가 존재하지 않았으며 계절별로 패턴이 다르게 나타났다. 이를 통해 EC 의 경우, 고정오염원이 아닌 차량 배출과 같은 이동오염원의 영향을 받음을 알 수 있었다. 이온 성분의 경우, 겨울철 질산염의 성분이 다른 계절에 비해 뚜렷한 증가를 나타내었다. 또한 이온 성분들의 당량비 계산 결과, 서울시 $PM_{2.5}$ 입자들은 약한 산성에 가까운 중성 입자인 것으로 나타났다. $PM_{2.5}$ 구성 성분들 간의 상관관계는 각 사이트별로 총 샘플링 기간에 대하여 피어슨 상관계수를 이용하여 구하였다. 그 결과 성분들 간 상관계수는 사이트별로 다양하게 나타났다. 특히 암모늄염과 황산염의 상관계수는 전반적으로 높게 나타났다 (r 평균 = 0.76). 암모늄염과 질산염 역시 전반적으로 높은

상관계수를 보였으나 (r 평균 = 0.63), 사이트에 따라 편차가 크게 나타났다 (0.57−0.86). 몇몇 사이트의 질산염 농도는 오히려 암모늄염보다 OC 와 높은 상관성을 보였다. 서울시 $PM_{2.5}$ 의 공간 변이성을 판단하기 위하여 서울시 19 개 사이트 측정값의 변이계수 (CV) 및 발산계수 (COD)를 구하였다. 그 결과, 디젤기관에서 주로 배출되는 EC 와 질산염이 다른 성분들에 비하여 공간적으로 불균일하게 분포하는 것을 알 수 있었다.

본 연구는 $PM_{2.5}$ 의 공간적 분포 특성에 대한 정보를 제공하고자, 서울시 19 개 지역에서 성능 검증 과정을 거친 DPIS 를 이용하여 동일한 방식으로 동시에 $PM_{2.5}$ 를 채취하였다. 본 연구 결과는 $PM_{2.5}$ 에 대한 개인의 노출 수준을 잘 대변할 수 있게 하여 추후 $PM_{2.5}$ 에 대한 건강영향 연구에 기여할 것으로 기대된다.

주요어 : $PM_{2.5}$, 소형 샘플러, 재현성, 정확성, 성분 분포, 공간 변이, 서울
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