

Seasonal Variation of PM_{2.5} and Its Major Ionic Components in an Urban Monitoring Site

Samik Ghosh, Zang-Ho Shon¹⁾, Ki-Hyun Kim*, Sang-Keun Song²⁾, Kweon Jung³⁾ and Nam-Jin Kim³⁾

Department of Environment and Energy, Sejong University, Seoul 143-747, Korea

¹⁾Department of Environmental Engineering, Dong-Eui University, Busan 614-714, Korea

²⁾Division of Earth Environmental System, Pusan National University, Busan 609-735, Korea

³⁾Seoul Metropolitan Government Institute of Public Health and Environment, Seoul, Korea

*Corresponding author. Tel: +82-2-3408-3233, E-mail: khkim@sejong.ac.kr

ABSTRACT

The ionic composition of PM_{2.5} samples was investigated by their datasets of cationic (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) and anionic components (Cl⁻, NO₃⁻, and SO₄²⁻) along with relevant environmental parameters collected from an urban monitoring site in Korea at hourly intervals in 2010. The mean (and SD) annual concentration of PM_{2.5} was computed as 25.3 μg m⁻³ with the wintertime maximum. In addition, sum concentrations (neq m⁻³) of five cationic species (291) were slightly lower than 3 anionic species (308). Most cations exhibited the highest seasonal values in spring, while anions showed more diversified seasonal patterns. According to PCA, five major source categories were apparent with the relative dominance of secondary inorganic aerosols (SIA). The results of our study suggest consistently that the distribution of ionic constituents in an urban area is affected by the combined effects of both natural and anthropogenic processes.

Key words: PM_{2.5}, Composition, Seasonal, Diurnal, Source apportionment

1. INTRODUCTION

As seen from elsewhere on the globe, many cities in Korea suffered from severe air pollution due to the combined effect of both local (e.g., vehicular traffic) and distant sources (e.g., transport from the industrial areas in China) (Han *et al.*, 2008). In an effort to reduce environmental problems associated with air pollution, the Korean Ministry of Environment (KMOE) established special act plan for the improvement of Metropolitan Air Quality on 1 January 2005. The main objective of such plan was to suppress the annual PM₁₀ levels from 60 (in 2005) to 40 μg m⁻³ (in 2014) (Heo

et al., 2009). However, in spite of various efforts, the PM_{2.5} levels in Seoul are still higher than many other cities in developed countries (Kim *et al.*, 2007).

In this study, eight major ionic components of PM_{2.5} including five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) plus three anions (Cl⁻, NO₃⁻, and SO₄²⁻) were measured routinely at hourly intervals over one year period (1st January to 31st December in 2010) at Gwang Jin Goo district of Seoul, Korea. Relevant parameters were also monitored concurrently to include both airborne criteria pollutants and basic meteorological parameters. Note that most of the previous studies of PM compositions had to rely on data sets collected over daily intervals. In this respect, our hourly measurement data should be useful enough to describe the short-term variability of ionic constituents. The data acquisition at such short interval should be important, as the air pollution in Seoul is heavily dependent on highly dynamic source activities (e.g., traffic conditions). These data sets were analyzed to describe the fundamental factors controlling the distribution of major ionic constituents in a number of aspects in relation to the changes in the relevant environmental parameters. The main objective of the present study is to investigate the seasonal variability of PM_{2.5} and its ionic constituents in air and to relate such results with its source/sink processes. The results of this study will thus help us gain valuable insights into the temporal variability of key chemical components of PM_{2.5} in an urbanized environment.

2. MATERIALS AND METHODS

In this study, ambient air samples were collected on a hourly basis for one year period (1st January to 31st December, 2010) at air quality monitoring station located at Goo Eui dong in Gwang Jin district (127° 05.44', 37° 32.40') of Seoul, Korea. Gwang Jin area, located

on the north side of the Han River of Seoul is home to couple of universities and many residential apartments along with a huge amusement park named as Children's grand park. Air quality of the area is known to be affected by traffic activities from adjacent roads without any major sources (Kim *et al.*, in press). The analysis of $PM_{2.5}$ and its ionic constituents was made continuously by a model ADI 2080 online analyzer (MARGA, Applikon Analytical B.V Corp., Netherlands). This system consists of a sampling box and an analytical box with the particle collection efficiency of 99.7%. Ambient air is drawn into the sampling box at a flow rate of $1 \text{ m}^3 \text{ h}^{-1}$ through the inlet. The gaseous components are also trapped by the liquid film (0.0035% H_2O_2) formed by one Wet Rotating Denuder (WRD). In the meantime, particles in residual airflow go through the supersaturated steam (0.0035% H_2O_2 , 120-140°C). They are erupted out from one Steam Jet Aerosol collector (SJAC) and pooled into its collector. These liquefied samples flow through glass filters, and are stored in syringe pumps of the analytical box for the final detection by Ion Chromatography (IC). As such, MARGA utilizes a WRD to collect acid gases and ammonia by diffusion into an aqueous film, while particles passing through the WRD are collected in a SJAC. A supersaturated environment is created within the SJAC which grows particles by a process known as deliquescence; it then allows them to be collected subsequently by inertial separation. As cooling takes place, steam condenses and washes the collected particles into an aqueous sample stream. The soluble ionic species in aqueous solutions from the WRD and SJAC are subsequently analyzed by IC (ion chromatography).

The method detection limit (MDL) was calculated for all ionic species. To calculate the MDL, a total of 25 mL volume solution was prepared for the IC analysis. From this total solution, 500 μL solution was used for NH_3 and each cations and 250 μL for the rest. The MDL was calculated as three times of standard deviation (SD) of the 7 replicate analyses. The obtained MDLs can be expressed in absolute mass (and equivalent concentration): for cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}), MDL values were 0.16 ng (0.35 neq m^{-3}), 0.16 ng (0.44 neq m^{-3}), 0.20 ng (0.26 neq m^{-3}), 0.20 ng (0.82 neq m^{-3}), and 0.16 ng (0.40 neq m^{-3}), respectively. The MDL values for anions (Cl^- , NO_3^- , and SO_4^{2-}) were 0.17 ng (0.47 neq m^{-3}), 0.17 ng (0.27 neq m^{-3}), and 0.08 ng (0.17 neq m^{-3}), respectively.

3. RESULTS AND DISCUSSION

3.1 General Tendency of $PM_{2.5}$ Concentration

In this research, the ionic components of $PM_{2.5}$ and

relevant parameters were monitored at Gwang Jin district of Seoul at hourly intervals from 1 January to 31 December, 2010. To facilitate the data analysis, daily mean values for all $PM_{2.5}$ constituents were computed: such values were acquired, only when more than two thirds of data are available for the day (e.g., > 18 hourly data). Hence, all the statistical treatment of data was basically made using these daily values, unless otherwise specified. The total number of daily values for different constituents was generally less than 340, as instruments were stopped occasionally either due to periodical maintenance or malfunctioning. Table 1 presents the summary of the cationic (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) and anionic (Cl^- , NO_3^- , and SO_4^{2-}) components of $PM_{2.5}$ measured in yearly and seasonal basis during the whole study period. The results are also computed for their derivatives (e.g., summation and ratio).

The annual concentration of $PM_{2.5}$ in our study was $25.3 \pm 16.0 \mu\text{g m}^{-3}$ which exceeded the US EPA annual standard of $15.0 \mu\text{g m}^{-3}$ (Table 2). The annual mean (\pm SD) concentrations of 5 cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) were 7.80 ± 6.90 , 212 ± 176 , 11.1 ± 13.6 , 14.3 ± 9.11 , and $39.5 \pm 28.7 \text{ neq m}^{-3}$, respectively. The concentrations for 3 anionic counterparts (Cl^- , NO_3^- , and SO_4^{2-}) were 13.5 ± 14.1 , 198 ± 99.9 , and $110 \pm 79.1 \text{ neq m}^{-3}$, respectively. To describe the fundamental aspects of their behavior and to validate the quality of our measurements, we checked for the extent of ionic balances using the molar concentration ratio between total cations and anions ($\sum \text{cations} / \sum \text{anions}$). The annual mean (and SD) of such ratios was less than unity (0.88 ± 0.43) (or cation deficiency) which may signify that the study site is slightly acidic (Fig. 1). All of the ionic components in $PM_{2.5}$ exhibited mo-

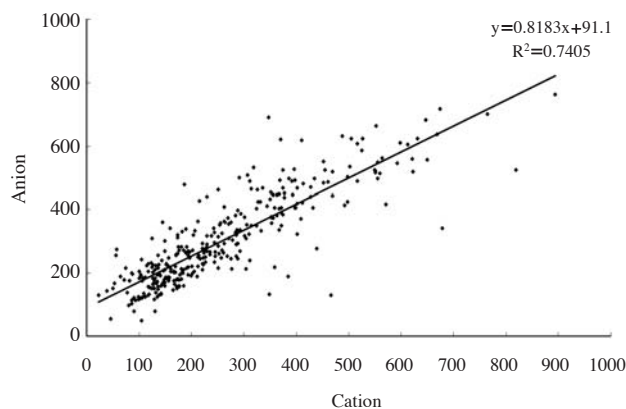


Fig. 1. Scattered plot of summation of cationic and anionic components of $PM_{2.5}$ at Gwang Jin, Seoul, Korea for the year 2010 excluding two outlying data on upper left and another two outlying data on lower right.

Table 1. Statistical summary of ionic components of PM_{2.5} measured at Gwang Jin district in Seoul, Korea during 2010.

Seasons	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	∑ Cations	∑ Anions	$\frac{\sum \text{Cations}}{\sum \text{Anions}}$
Spring	10.3±8.45 (7.83) ^a	217±132 (194)	11.2±5.62 (9.83)	16.3±9.18 (14.0)	49.3±19.7 (46.5)	15.7±8.91 (14.7)	220±98.3 (203)	120±79 (101)	92±144 (284)	345±154 (327)	0.85±0.13 (0.85)
	2.75-55.2 (87) ^b	30.7-659 (87)	4.17-32.6 (87)	4.75-57.6 (87)	19.5-137 (87)	2.21-52.4 (87)	96.6-843 (87)	15.8-486 (87)	45.9-893 (87)	56.8-946 (87)	0.28-1.18 (87)
Summer	6.91±3.41 (6.18) ^a	210±165 (162)	8.18±4.78 (6.81)	12.7±8.26 (9.6)	46.3±27.2 (37.5)	6.12±4.38 (5.00)	180±58.5 (168)	133±92.1 (104)	270±161 (227)	305±128 (256)	0.89±0.53 (0.85)
	2.45-18.7 (89) ^b	22.4-920 (91)	2.24-27.1 (91)	3.77-37.2 (91)	7.33-125 (91)	0.78-25.0 (91)	21.0-346 (91)	11.7-405 (91)	53.1-765 (91)	94.2-701 (91)	0.21-5.14 (91)
Fall	4.87±3.61 (3.66) ^a	230±255 (145)	13.2±24.9 (7.23)	13.1±7.49 (11.5)	33.6±43.3 (22.8)	4.32±3.57 (3.10)	169±88.5 (152)	94.0±72.3 (67)	286±272 (177)	263±145.7 (218)	1.03±0.65 (0.96)
	2.13-25.0 (75) ^b	17.8-1397 (75)	1.73-192 (75)	3.46-37.3 (75)	2.93-278 (75)	1.01-19.6 (72)	4.10-433 (75)	2.70-363 (74)	22.9-1526 (75)	50.9-718 (74)	0.18-4.14 (74)
Winter	8.78±8.78 (6.54) ^a	194±140 (151)	11.9±11.1 (9.68)	15.1±10.7 (13.1)	27.5±12.2 (26.1)	26.6±18.9 (25.7)	218±132 (179)	89.0±60.7 (71)	237±126 (202)	314±175.7 (290)	0.78±0.16 (0.81)
	2.00-53.8 (86) ^b	21.8-776 (86)	2.43-98.1 (86)	4.59-73.5 (86)	10.6-68.0 (86)	1.71-112 (86)	72.9-891 (86)	14.9-398 (86)	80.5-646 (86)	99.7-1101 (86)	0.39-1.1 (86)
All	7.80±6.90 (6.20) ^a	212±176 (162)	11.1±13.6 (8.72)	14.3±9.11 (12.0)	39.5±28.7 (32.9)	13.5±14.1 (8.67)	198±99.9 (175)	110±79.1 (90.0)	271±181 (223)	308±154 (269)	0.88±0.43 (0.85)
	2.00-55.2 (337) ^b	17.8-1397 (339)	1.73-192 (339)	3.46-73.5 (339)	2.93-278 (339)	0.78-113 (336)	4.10-891 (339)	2.69-486 (338)	22.9-1526 (339)	50.9-1101 (338)	0.18-5.14 (338)

^aMean ± SD (median); and ^bRange (number of observations).**B. Test of statistical significance for seasonal dominance.**

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	∑ Cations	∑ Anions	$\frac{\sum \text{Cations}}{\sum \text{Anions}}$
χ ²	1.12	0.42	0.41	0.82	0.84	4.84	3.22	0.99	0.17	1.20	1.45
P	0.26	0.68	0.68	0.41	0.40	1.28E-06	1.26E-03	0.32	0.86	0.23	0.15

^cZ statistics is used to check the statistical significance of seasonal peak values by comparing between the highest mean value and the one next to it.

Table 2. Statistical summary of ionic components of PM_{2.5}, PM₁₀, and environmental parameters measured concurrently at Gwang Jin district in Seoul, Korea during 2010

Seasons		PM ₁₀	PM _{2.5}	SO ₂	NO ₂	NO _x	CO	O ₃	WS	TEMP	HUM	UV
Unit		(µg/m ³)										
		(ppb)										
Spring	51.1±26.9 (48.25) ^a	24.0±11.0 (22)	3.61±1.45 (3.33)	32.2±10.8 (31.4)	42.7±16.9 (39.7)	501±126 (508)	31.0±10.4 (30)	2.30±0.77 (2.21)	10.8±5.92 (9.6)	61.0±14.1 (59.08)	0.57±0.25 (0.63)	
	7.63-137 (87) ^b	3.70-60.0 (87)	1.63-10.6 (87)	12.1-54.7 (87)	14.3-84.9 (87)	192-806 (87)	9.71-68.8 (87)	1.10-5.93 (87)	-0.73-22.5 (87)	28.7-97 (87)	0.08-1.13 (87)	
Summer	35.4±21.1 (31.83) ^a	22.0±15.0 (19)	2.78±0.75 (2.63)	28.6±8.6 (28.3)	37.6±10.9 (35.9)	544±134 (553)	28.0±13.7 (27)	1.80±0.29 (1.79)	25.7±2.14 (26.1)	74.7±11.6 (76.46)	0.67±0.23 (0.7)	
	8.00-141 (91) ^b	4.53-100 (91)	1.71-5.3 (91)	13.9-51.6 (91)	17.4-67.6 (91)	254-875 (91)	4.42-64.7 (88)	1.00-2.53 (91)	18.5-29.4 (91)	38.4-93.0 (91)	0.10-1.10 (91)	
Fall	47.6±33.8 (39.54) ^a	25.0±23.0 (19)	3.63±1.50 (3.6)	30.3±10.2 (30.9)	52.7±24.9 (52.8)	580±145 (575)	16.0±6.8 (16)	2.00±0.78 (1.65)	12.6±6.17 (13.4)	64.9±13.9 (66.96)	0.56±0.19 (0.55)	
	7.54-192 (75) ^b	4.47-136 (75)	1.25-8.80 (75)	10.9-53.8 (75)	14.3-119.4 (75)	208-871 (73)	2.40-34.1 (75)	1.22-5.23 (75)	-0.64-25.3 (75)	27.9-96.0 (75)	0.10-0.95 (74)	
Winter	55.9±24.8 (51.33) ^a	29.0±14.0 (26)	5.54±1.52 (5.54)	36.2±12.3 (34.5)	63.6±29.3 (63.2)	562±163 (573)	13.0±7.6 (12)	2.20±0.89 (1.91)	-0.85±5.56 (-1.3)	61.1±14.3 (61.1)	0.36±0.13 (0.39)	
	5.30-149 (89) ^b	3.28-81 (89)	1.92-10.5 (89)	13.1-66.5 (89)	16.0-120.5 (89)	133-878 (88)	1.17-30.8 (89)	1.05-4.92 (89)	-11.6-13.6 (89)	31.6-97 (89)	0.03-0.59 (89)	
All	47.4±27.7 (43.0) ^a	25.3±16.0 (21.8)	3.89±1.68 (3.46)	31.9±10.9 (30.7)	49.0±23.7 (42.9)	546±145 (550)	22.3±12.5 (21.1)	2.08±0.75 (1.88)	12.2±11.0 (11.8)	65.5±14.6 (66.9)	0.54±0.24 (0.51)	
	5.30-192 (342) ^b	3.28-136 (342)	1.25-10.6 (342)	10.9-66.5 (342)	14.3-121 (342)	133-878 (339)	1.17-68.8 (339)	1.00-5.93 (342)	-11.7-29.4 (342)	27.9-96.9 (342)	0.03-1.13 (341)	

^aMean ± SD (median); and ^bRange (n).

B. Test of statistical significance for seasonal dominance.

	PM ₁₀	PM _{2.5}	SO ₂	NO ₂	NO _x	CO	O ₃	WS	TEMP	HUM	UV
χ ²	1.23	1.27	8.08	2.33	2.58	0.60	1.40	1.07	17.54	4.88	2.90
P	0.22	0.21	6.66E-16	0.02	0.01	0.55	0.16	0.28	0.00	1.07E-06	3.69E-03

χ² statistics is used to check the statistical significance of seasonal peak values by comparing between the highest mean value and the one next to it.

derate variation with their relative standard error (RSE) less than 10% (i.e., maximum of 6.67% in case of K⁺). The concentrations of criteria pollutants (SO₂, NO₂, NO_x, CO, and O₃) averaged as 3.89 ± 1.68, 31.9 ± 10.9, 49.0 ± 23.7, 546 ± 145, 22.3 ± 12.5 ppb, respectively. During the year 2010, temperature and humidity data averaged 12.2 ± 11.0°C and 65.5 ± 14.6%, respectively.

Although the results of PM_{2.5} analysis are not consistent enough to cover various locations throughout Korea, gradual reductions in PM_{2.5} levels across decadal

periods are fairly apparent between different studies. The concentration of PM_{2.5} was measured as 44.2 µg m⁻³ in Chongju, Korea in 1995-1996 (Hieu and Lee, 2010). The PM_{2.5} values were measured as 27.6 µg m⁻³ in Ulsan in 2008 (Hieu and Lee, 2010). It's concentration in Daejeon, another major city of Korea was 37.7 ± 17.2 µg m⁻³ in 2008 (Lim *et al.*, 2011). In relatively clear areas like Deokjeok and Gosan in Korea concentrations of PM_{2.5} were somewhat comparable with our data such as 25.3 ± 22.6 and 17.2 ± 10.8 µg m⁻³, respectively, during the period 2005-2007 (Kim

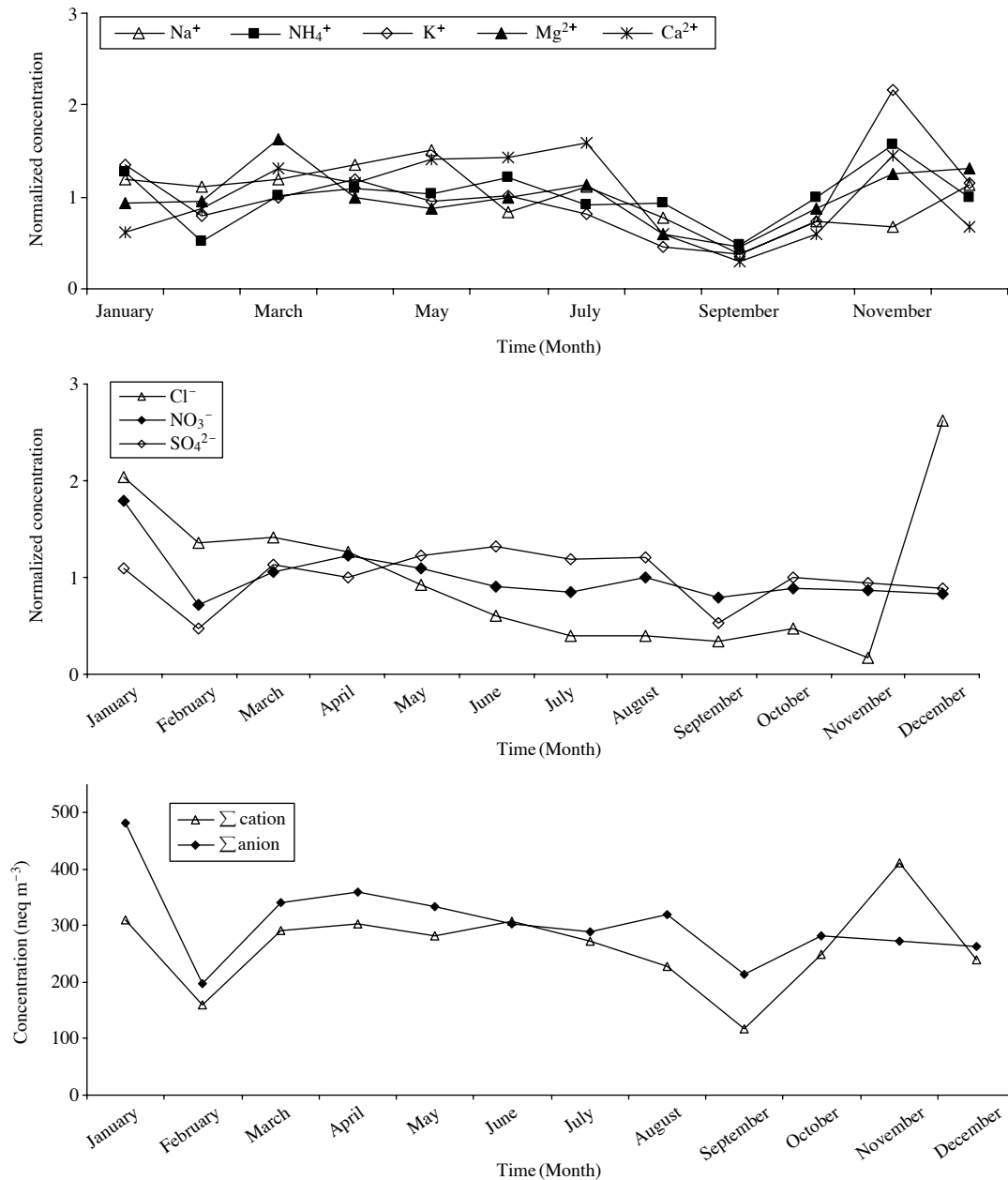


Fig. 2. Normalized monthly distribution of ionic components of PM_{2.5} at Gwang Jin district in Seoul, Korea during 2010.

et al., 2009). It is important to note that over the years, PM_{2.5} has decreased consistently across Korea. Thus, it is not necessarily uncommon to find less PM_{2.5} values in our experiment than the old studies.

3.2 Seasonal Variation of PM_{2.5} Constituents

As the distribution of PM_{2.5} is known to exhibit strong seasonal variations, so we may expect such pattern from its diverse constituents (Fig. 2). In order to have a thorough understanding of the temporal pattern between different ionic constituents, the seasonal patterns of PM_{2.5} and its constituents were examined. The PM_{2.5} concentration at our study site was the highest in winter with the value of $29 \pm 14 \mu\text{g m}^{-3}$ (range 3.28–81) (Table 2). Such wintertime enhancement in PM_{2.5} levels is comparable to those seen in many previous findings in Korea (Kim *et al.*, 2004). It is interesting to note that all of the criteria pollutants (namely PM₁₀, PM_{2.5}, SO₂, NO₂, NO_x, and CO), except O₃ consistently show wintertime maxima. The observed pattern in our study might also reflect the combined effects of source mechanisms (the use of fossil fuel for house heating and cold start of car engines) and meteorological conditions (e.g., reduced mixing heights in winter and enhanced wet depositions during summer) (Kim *et al.*, 2007). In addition, enhanced PM levels (mainly crustal components) are commonly observed in the spring months (March and April) due to the common occurrences of Asian Dust (AD) event (Kim *et al.*, 2003). However, in our study period of 2010, such signals were not strong enough.

According to our analysis, most ionic species tend to exhibit strong seasonality across four seasons, namely spring (March to May), summer (June to August), fall (September to November), and winter (December to February). Although some cations (Na⁺, Mg²⁺, and Ca²⁺) showed their peak occurrences in spring, others (NH₄⁺ and K⁺) did in fall. However, this seasonal dominance is not statistically significant, if comparison is made between the highest seasonal mean and the one next to it (by the z statistics test at $p < 0.05$). The observed fall peak of NH₄⁺, although insignificant statistically, is different from the finding of Lee *et al.* (1999) who reported winter time maximum in Seoul.

The concentrations of anions (Cl⁻, NO₃⁻, and SO₄²⁻) exhibited more diversified patterns with their maximum in winter (26.6), spring (22.0), and summer (133 neq m⁻³), respectively. The seasonal patterns of the former two are statistically significant, while it is not the case for SO₄²⁻. The highest nitrate concentration is observed in spring closely followed by winter in our study. This is somewhat unusual, as it tends to peak in winter by enhanced consumption of fossil fuel and increased NO_x levels. It is known that nitrate in the atmo-

sphere can result mainly from the atmospheric conversion of nitrogen gases (NO and NO₂) and ammonia (NH₃) (Seinfeld and Pandis, 1998). Moreover, the partitioning of inorganic NO₃⁻ (from HNO₃ and ammonium nitrate) is generally favored in cold weather (Khan *et al.*, 2010). As such, its minimum values are typically observed in summer (Lee *et al.*, 1999).

As a secondary pollutant, SO₄²⁻ was found to be the highest in summer. This pattern of SO₄²⁻ appears to be a common trend in many previous studies conducted elsewhere (Khan *et al.*, 2010). This relative sulfate enhancement in summer can be attributed at least partially to such effect as increased photochemical activity (Husain and Dutkiewicz, 1990). In addition, sea salt emission may also make a certain contribution to the total SO₄²⁻ concentration, if one considers the distance between the study site and seashore (35 km). However, its winter time enhancement associated with high coal combustion was also reported (Cyrus *et al.*, 1995). Sulphate is suspected to come from long-range transport as well as regional sources (Yao *et al.*, 2002). Our wintertime maximum of Cl⁻ concentration appears to match with the seasonal pattern seen in China (Yao *et al.*, 2002). It is well known that high concentration of Cl⁻ in the winter months is known to be associated with coal burning. Despite the observed complexities among individual ionic components, the sum concentrations of both cationic and anionic components peaked consistently in spring (292 and 345 neq m⁻³, respectively). It is also interesting to find that the sum ionic ratios ($\sum \text{cations} / \sum \text{anions}$) were the highest in fall (1.03 ± 0.65) but the lowest in winter (0.78 ± 0.16). This observation may signify the fact that overall deviation from the unity in its ratio should have proceeded most significantly during winter with increased acidity.

3.3 Factors Controlling the Distribution of PM_{2.5} and Its Constituents

There are many factors that can exert controls on the distribution of PM_{2.5} and its ionic constituents. To learn more about the relationship between those components, their correlation patterns were examined by using their daily mean data on both yearly and seasonal intervals. Results shown in Table 3 indicate the frequent occurrences of strong correlations between many cationic and anionic species. Among the cations, NH₄⁺ shows strong correlation with most cations (except Mg²⁺) and all anions; this trend is seen consistently throughout the seasons. Among the anions, SO₄²⁻ is strongly correlated with most cations in all seasons, while maximum frequency of strong correlation is observed in spring (Fig. 2). It is seen that Na⁺ also shows a strong correlation with Cl⁻ ($r=0.31$, $p=5.44\text{E-}09$), suggesting the possible role of sea salt (NaCl) as the PM_{2.5} source. If

Table 3. Correlation analysis using daily mean values of chemical components of PM_{2.5} at Gwang Jin district in the year 2010.

A. Using all data collected in 2010.

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	∑ Cations	∑ Anions	∑ Cations+ ∑ Anion	PM ₁₀
Na ⁺	r	1										
NH ₄ ⁺	p	0.18**	1									
K ⁺	p	1.15E-03	0.38**	1								
Mg ²⁺	p	4.24E-04	8.67E-13	0.28**	1							
Ca ²⁺	p	0.46**	0.13*	2.64E-07	0.43**	1						
Cl ⁻	p	4.08E-19	0.02	0.20**	1.22E-16	4.11E-10	1					
NO ₃ ⁻	p	4.70E-07	1.16E-05	2.03E-04	0.21**	0.33**	0.52**	1				
SO ₄ ²⁻	p	0.31**	0.26**	0.13*	1.25E-04	0.13*	5.26E-25	0.80**	1			
∑ Cations	p	5.44E-09	1.33E-06	0.01	1.25E-04	0.24**	0.46**	1.14E-75	0.76**	1		
∑ Anions	p	1.53E-06	7.13E-167	9.35E-17	1.49E-07	6.46E-06	7.43E-19	1.14E-75	0.90**	0.93**	1	
∑ Cations+	p	0.20**	0.74**	0.18**	0.08	0.34**	0.90**	0.76**	0.76**	0.93**	0.93**	1
∑ Anions	p	3.17E-04	5.48E-60	1.06E-03	0.13	1.28E-10	1.15E-121	1.45E-65	7.87E-64	0.92**	0.92**	1
PM ₁₀	p	0.25**	0.89**	0.33**	0.20**	0.31**	0.73**	0.83**	5.98E-143	0.54**	0.66**	1
	p	3.76E-06	3.10E-115	4.05E-10	1.72E-04	9.32E-09	1.54E-56	1.84E-88	1.54E-27	1.03E-50	6.65E-44	
	p	0.28**	0.74**	0.38**	0.26**	0.35**	0.40**	0.64**	0.70**	0.70**	0.70**	
	p	1.09E-07	1.14E-60	3.29E-13	1.96E-06	5.06E-11	1.79E-14	1.24E-39	1.03E-50	1.54E-27	6.65E-44	

*Correlation is significant at 0.05 level of significance.

** Correlation is significant at 0.01 level of significance.

B. Evaluation of correlation frequency on a seasonal scale.

Class	Seasons				Oveall
	Spring	Summer	Fall	Winter	
No class ^a	17	23	30	37	20
I ^b	9	5	13	5	3
II ^c	17	14	5	5	14
III ^d	6	10	5	3	4
IV ^e	17	14	13	16	25

^a=P ≥ 10⁻³

^b=10⁻³ ≤ P < 10⁻³

^c=10⁻¹⁰ ≤ P < 10⁻⁵

^d=10⁻¹⁵ ≤ P < 10⁻¹⁰

^e=P < 10⁻¹⁵

relationships between different parameters are examined carefully, several interesting trends emerge. The observed correlation of NH_4^+ with SO_4^{2-} ($r=0.85$, $p=1.22\text{E-}94$) and NO_3^- ($r=0.50$, $p=7.33\text{E-}23$) may imply similarities in their emission sources. A strong correlation of SO_4^{2-} with NH_4^+ (relative to NO_3^-) also suggests a preferential formation of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 over more volatile NH_4NO_3 . Direct emissions (e.g., NO_2 , SO_2 , CO , and PM_{10}) from motor vehicles are often explained in relation to traffic flow in Korea (Kim and Guldmann, 2011). Because diesel vehicles are still one of the major sources of SO_2 emission in urban areas of Korea (Korea Ministry of Environment, 2011), higher concentration of SO_4^{2-} can be maintained throughout the day. The concentration data of NH_4^+ show strong correlations with many other parameters (e.g., Σ cation (0.95), Σ anion (0.74), Σ all ions (0.89), and PM_{10} (0.74)). It is thus reasonable to infer that NH_4^+ should be influenced by emissions from many anthropogenic sources in urban areas. In atmosphere, Ca^{2+} is generally believed to originate from soil, crustal material (e.g., calcite and dolomite), or construction activities (e.g., cement manufacturing). In our study, a strong correlation has been observed between Ca^{2+} and Mg^{2+} ($r=0.43$, $p=1.22\text{E-}16$). The relationship between Ca^{2+} and SO_4^{2-} ($r=0.24$, $p=8.48\text{E-}06$) also suggests the formation of CaSO_4 . Interestingly, a strong correlation ($r=0.52$, $p=5.26\text{E-}25$) between two anions namely NO_3^- and SO_4^{2-} can be highly significant, if they exist as internal mixtures or if their concentrations are governed by common meteorological conditions (Zhuang *et al.*, 1999).

The results of our correlation analysis were also evaluated after being divided into five different classes based on the magnitude of probability (P) such as: (1) no class (the weakest correlation range); $P \geq 10^{-3}$; (2) class I (moderately weak correlation); $10^{-5} \leq P < 10^{-3}$; (3) class II ($10^{-10} \leq P < 10^{-5}$); (4) class III ($10^{-10} \leq P < 10^{-5}$); and (5) class IV (the strongest correlation range): $P < 10^{-15}$. The results of this comparative analysis are summarized to allow direct comparison among different seasons (Table 3b). If we go through the correlation results derived from all yearly data, it is seen that among 66 matching pairs for each data group, the frequency of the strongest correlation pairs (IV) is the highest among all five classes for comparison. It is also seen that among 66 cases, majority of the values are found either in Class II (14), no class (20), and class IV (25). Among the seasonally grouped data sets, the strongest correlation pairs (IV) are found most frequently in spring with 17 out of 66 cases. In contrast, the least significant correlation case (no class) was dominant in winter with 37 out of 66 cases.

3. 4 Source Identification of Constituents of $\text{PM}_{2.5}$ using PCA

For the effective management of air quality, it is important to characterize the sources of target pollutants. The fine particles are a mixture of primary and secondary (mainly anthropogenic origin) aerosols through vapor nucleation/condensation mechanisms (Kleeman and Cass, 1998). To learn more about the processes controlling the ionic composition of $\text{PM}_{2.5}$, it is meaningful to assess relative contribution between different sources (Manoli *et al.*, 2002).

Factor analysis (FA) is a useful tool to assess the relative roles between different emission sources without the aid of local source profile library. As part of FA, we conducted principal component analysis (PCA) (using SPSS v16) with varimax rotation using the daily average data of each constituent. As a type of multivariate analysis, PCA has been widely employed in air quality studies. The results yielded five source components, namely PC1 through PC5 which accounted for 30.6, 14.0, 13.3, 10.3, and 7.89% of the total variance (Table 4). To simplify the interaction among the ions, only the positive r values are considered. PC1 is identified as secondary inorganic aerosol (SIA) component with high 'r' values of NH_4^+ (0.90), NO_3^- (0.80), and SO_4^{2-}

Table 4. Results of principal component analysis (PCA) with varimax rotation by using $\text{PM}_{2.5}$ chemical component data the daily mean at Gwang Jin district in Seoul, Korea during 2010^a.

Component	1	2	3	4	5
% of variance	30.6	14.0	13.3	10.3	7.89
Na^+	0.22	–	0.19	0.57	0.11
NH_4^+	0.90	0.23	1.24E-03	0.18	–
K^+	0.16	0.25	0.05	0.53	0.13
Mg^{2+}	0.05	–	0.22	0.78	0.02
Ca^{2+}	0.11	–	–	0.72	–0.04
Cl^-	0.27	0.15	0.67	0.10	0.11
NO_3^-	0.80	0.10	0.24	–	–
SO_4^{2-}	0.88	0.04	–	0.23	–
Σ Cations	0.86	0.17	–	0.36	–
Σ Anions	0.94	0.07	0.13	–	–
Σ Cations+	0.95	0.13	0.05	0.18	–
Σ Anions	–	–	–	–	–
PM_{10}	0.66	0.25	0.21	0.32	0.32
$\text{PM}_{2.5}$	0.79	0.33	0.12	0.23	0.13
SO_2	0.44	0.27	0.53	0.13	0.42
NO_2	0.47	0.73	0.19	1.31E-03	0.21
NO_x	0.29	0.80	0.38	–	0.14
CO	0.43	0.66	0.18	0.03	–
O_3	0.13	–	–	0.12	0.13
WS	–	–	0.22	0.18	0.30
TEMP	0.07	0.07	–	–	–
HUM	0.17	0.15	–	–	–
UV	–	–	–	–	0.37

^aRotation converged in 7 iterations.

(0.88) along with their summation terms. To have a better understanding of sources, PCA was performed on a seasonally divided data groups as well. The results showed the highest variance in summer (84.3%), followed by spring (82.6%), winter (79.5%), and fall (76.7%). In each season, their main source was identified as secondary inorganic aerosol with the highest variance in spring (38.2%), followed by fall (36.2%), summer (34.6%), and winter (29.1%). In a recent study conducted at Corpus Christi, an industrial and coastal city in South Texas, US, secondary sulphate was also identified as the dominant source category (30.4%) of the apportioned mass which is comparable with our value of 30.6% (Karnae and John, 2011). A predominance of such sources as soil dust, traffic, oil/coal combustion, and road dust was seen in outdoor microenvironment in Daejeon, one of the major cities in Korea (Lim *et al.*, 2011).

The second main source (PC2) appears to be affected by the secondary nitrate with high 'r' value of NO₂ (0.73), NO_x (0.80), and CO (0.66). In all seasons (except summer), secondary nitrate became the second main source. However, in summer, second source was identified as road dust with high r value of Na⁺ (0.71), K⁺ (0.64), Mg²⁺ (0.86), and Ca²⁺ (0.89). Third source (PC3) was unidentified with high r value of Cl⁻ (0.67) and SO₂ (0.53). This source seems to be little ambiguous to a degree, although both SO₂ and Cl⁻ can be generated from traffic emission. Hence, traffic activities can act as the source of this component. The fourth main source (PC4) was identified as the road dust with high r values of Na⁺ (0.57), K⁺ (0.53), Mg²⁺ (0.78), and Ca²⁺ (0.73). Road dust normally originates from multiple sources such as automobile exhaust, lubricating oil residues, tire and brake lining wear, street surface weathering, leaf detris, garden soil, etc (Rogge *et al.*, 1993). In Mexico City, vehicular emission was also estimated as the most important source of PM_{2.5} in an urban site (42%), followed by re-suspended dust (26%), secondary inorganic aerosols (11%), and industrial emission and food cooking (10% each). Result of factor analysis in Jeju Island, Korea indicated the existence of at least three major sources including sea-salt aerosol, secondary aerosol, and organic aerosol component in 1997 (winter) and 1998 (spring) (Kim *et al.*, 2002). The observed difference between Jeju and our study may be explained by the fact that the target site in Jeju is a relatively clean area with low anthropogenic activities.

4. CONCLUSIONS

In order to describe the distribution characteristics of PM_{2.5} and its ionic constituents, we analyzed their

hourly data sets initially collected at hourly intervals for one year period in 2010. The seasonal distribution of PM_{2.5} pattern in our study was generally characterized by its maximum in winter. The concentration of cationic components normally peaked in spring, while their anionic counterparts showed more diversified patterns. The seasonal variation of most ions was rather insignificant statistically, in terms of z test between the highest mean value and the one next to it.

When our data were examined by correlation analysis, the results indicated that most of the inorganic ion pairs maintained significant correlation. The results of PCA showed the existence of 5 major sources with the dominance of secondary inorganic aerosols (SIA). Thus, the results of our study, if analyzed in relation with seasonal and diurnal groups demonstrate consistently that the hourly data measured during the study period can be closely tied with the signatures of both natural and anthropogenic processes.

REFERENCES

- Cyrus, J., Gutschmidt, K., Brauer, M., Dumyahn, T., Heinrich, J., Spengler, J.D., Wichmann, H.E. (1995) Determination of acidic sulfate aerosols in urban atmospheres in Erfurt (F.R.G.) and Sokolov (Former C.S.S.R.). *Atmospheric Environment* 29(23), 3545-3557.
- Han, Y.J., Kim, T.S., Kim, H. (2008) Ionic constituents and source analysis of PM_{2.5} in there Korean cities. *Atmospheric Environment* 42, 4735-4746.
- Heo, J.-B., Hopke, P.K., Yi, S.-M. (2009). Source apportionment of PM_{2.5} in Seoul, Korea. *Atmospheric Chemistry and Physics* 9, 4957-4971.
- Hieu, N.T., Lee, B.K. (2010) Characteristics of particulate matter and metals in the ambient air from a residential area in the largest industrial area in Korea. *Atmospheric Research* 98, 526-537.
- Husain, L., Dutkiewicz, V.A. (1990) A long term (1975-1988) study of atmospheric SO₄²⁻: regional contributions and concentration trends. *Atmospheric Environment* 24A, 1175-1187.
- Karnae, S., John, K. (2011) Source apportionment of fine particle matter measured in an industrialized coastal area of South Texas. *Atmospheric Environment* 45, 3769-3776.
- Khan, M.F., Shirasuna, Y., Hirano, K., Masunaga, M. (2010) Characterization of PM_{2.5}, PM_{2.5-10} and PM_{>10} in Ambient Air, Yokohama, Japan. *Atmospheric Research* 96, 159-172.
- Kim, H.S., Huh, J.B., Hopke, P.K., Holsen, T.M., Yi, S.M. (2007) Characteristics of the major chemical constituents of PM_{2.5} and smog events in Seoul, Korea in 2003 and 2004, *Atmospheric Environment* 41(32), 6762-6770.
- Kim, K.H., Lee, M., Lee, G., Kim, Y.P., Youn, Y.H., Oh, J.M. (2002) Observations of aerosol-bound ionic compositions at Cheju Island, Korea. *Chemosphere* 48,

- 317-327.
- Kim, K.-H., Ho, D.-X., Park, C.-G., Ma, C.-J., Pandey, S.K., Lee, S.C., Jeong, H.J., Lee, S.H. (2012) Volatile organic compounds in ambient air at four residential locations of Seoul, Korea. *Environmental Engineering Science*. In Press.
- Kim, K.W., He, Z., Kim, Y.J. (2004) Physico-chemical characteristics and radiative properties of Asian dust particles observed at Kwangju, Korea during the 2001 ACF-Asia IOP. *Journal of Geophysical Research* 109, D19S01-D19S02.
- Kim, K.-H., Choi, G.-H., Kang, C.-H., Lee, J.-H., Kim, J.Y., Youn, Y.H., Lee, S.R. (2003) The chemical composition of fine and coarse particles in relation with the Asian Dust events. *Atmospheric Environment* 37, 753-765.
- Kim, Y., Guldmann, J.-M. (2011) Impact of traffic flows and wind directions on air pollution concentrations in Seoul, Korea. *Atmospheric Environment* 45, 2803-2810.
- Kim, Y.-J., Woo, J.-H., Ma, Y.-I., Kim, S., Nam, J.-S., Sung, H., Choi, K.-C., Seo, J., Kim, J.-S., Kang, C.-H., Lee, G. (2009) Chemical characteristics of long-range transport aerosol at background sites in Korea. *Atmospheric Environment* 43, 5556-5566.
- Kleeman, M.J., Cass, G.R. (1998) Source contributions to the size and composition distribution of urban particulate air pollution. *Atmospheric Environment* 32(16), 2803-2816.
- Korea Ministry of Environment (2011) http://eng.me.go.kr/content.do?method=moveContent&menuCode=pol_c_ha_air_pol_tra_status.
- Lee, H.S., Kang, C.-M., Kang, B.-W., Kim, H.-K. (1999) Seasonal variations of acidic air pollutants in Seoul, South Korea. *Atmospheric Environment* 33, 3143-3152.
- Lim, J.-M., Jeong, J.-H., Lee, J.-H., Moon, J.-H., Chung, Y.-S., Kim, K.-H. (2011) The analysis of PM_{2.5} and associated elements and their indoor/outdoor pollution status in an urban area. *Indoor Air* 21, 145-155.
- Manoli, E., Voutsas, D., Samara, C. (2002) Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmospheric Environment* 36, 949-961.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R.T. (1993). Quantification of urban organic aerosols at a molecular-level-identification, abundance and seasonal-variation. *Atmospheric Environment Part a-General Topics* 27, 1309-1330.
- Seinfeld, J.H., Pandis, S.N. (1998) *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1st edition, J. Wiley, New York.
- Yao, X., Chan, C.K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., Ye, B. (2002) The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China. *Atmospheric Environment* 36, 4223-4234.
- Zhuang, H., Chan, C.K., Fang, M., Wexler, A.S. (1999) Size distribution of particulate sulfate, nitrate, and ammonium at a coast site in Hong Kong. *Atmospheric Environment* 33, 848-853.

(Received 24 November 2011, revised 9 February 2012, accepted 9 February 2012)