Chemical Composition of the Ambient $PM_{2.5}$ in 2014 over Korea

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Abstract

$PM_{2.5}$ samples were collected in the Seoul, Daejeon, Gwangju, Baengnyeong, Jeju and Ulsan areas in 2014. Water-soluble ions, elements and carbonaceous $PM_{2.5}$ species were analyzed and the concentration distribution and seasonal characteristics were investigated. The annual mean concentrations of $PM_{2.5}$ were 25.9, 28.1, 27.4, 24.1, 15.5, 22.4 μg/m^3 in Seoul, Daejeon, Gwangju, Baengnyeong, Jeju and Ulsan, respectively. Water-soluble inorganic ions accounted for 52.9 to 61.3% of the total $PM_{2.5}$ mass concentrations. Sulfate, nitrate and ammonium were the major water-soluble ions in the aerosols. The elemental compositions were dominated by potassium, calcium and iron, and the proportion of total elemental components ranged from 6.3 to 8.2% in the $PM_{2.5}$ mass concentrations. The annual average contribution of TC (Total carbon) to $PM_{2.5}$ mass ranged from 18.3 to 26.6%. Iron, lead and zinc constituted the main elements in these fine particles. In the case of ions, NH_4^+, NO_3^-, and SO_4^{2-} exhibited much variation according to season. As for the seasonal characteristics of elements, most regions showed high concentrations of crustal elements in spring. Organic carbon concentrations were generally higher in winter than in summer.

Key words: ambient $PM_{2.5}$, carbonaceous aerosol, chemical composition, elemental components, water-soluble ions

1. Introduction

Atmospheric PM (particulate matter) is currently one of the most vexatious environment problems, with adverse effects on human health and climate change. To limit these adverse impacts and develop efficient strategies for air quality control, knowledge of the chemical composition of $PM_{2.5}$ is needed (Salameh *et al*., 2015). Particulate matter can be divided into two kinds, namely, primary emissions generated directly from sources such as manufacturing industries, car emissions, coal combustion, resuspended road dust, waste incineration and biomass burning; and secondary production generated through reactions between the primary emissions in the gaseous phase and ammonia, ozone, VOCs, etc. in the atmosphere. According to the 'KORUS-AQ Campaign' (Korea-United States Air Quality Study) conducted in Seoul and other metropolitan areas in May-June 2016, secondary production accounted for more than three-quarters of fine particle pollutants observed during the study. The overall composition is dominated by organics, but sulfates and nitrates still comprise nearly half of the secondary aerosol mass. Local gradients and correlations between fine aerosol and other chemical indicators suggest that local sources make a dominant contribution to secondary aerosol production. (NIER, 2017) In the Seoul Metropolitan Area, the proportion of PM concentration due to secondary production is increasing; therefore studies are needed to determine whether this is due to reactions with locally emitted precursors, or due to influx from the outside. Particulate matter is not a single kind of substance, but an aggregate with a wide range of sizes and diverse chemical components depending on how it was generated by the primary emissions or secondary production phase. Thus a scientific understanding of efficient reduction and management of particulate matter should be preceded by a scientific understanding of the processes by which various types of particulate matter are emitted, produced, converted, carried to other places and destroyed, and of the effects of particulate matter on human health, ecosystems, climate change and political administration (KAST, 2016).

The main components of $PM_{2.5}$ in the atmosphere are water-soluble ions, elemental carbon (EC), organic carbon (OC), elements, organic matter, and so on. Elements comprise crustal elements such as Si, K and Ca, while Ti, Mn, Fe and Mn are marker elements of anthropogenic sources such as the steel industry, road dust and brake-wear dust. There are also trace elements that come from artificial emission sources such as As, Se, V, Cr, Ni, Cd and Pb. They are a crucial factor in the origination and long-range movement of air pollutants, and their type and concentration profile vary according to the emission source (Sung *et al.*, 2015). Water-soluble ions mainly include NO_3^-, SO_4^{2-}, and NH_4^+, and account for at least 50% of $PM_{2.5}$ components, while carbonaceous components account for approximately 20% or more of $PM_{2.5}$ (NIER, 2014a; Jeon *et al.*, 2015).

The Republic of Korea has set and applied ambient air quality standards for $PM_{2.5}$ specifying an annual average of 25 μg/m^3 and daily average of 50 μg/m^3 since 2015. The Enforcement Decree of the Framework Act on Environmental Policy, which strengthened the air quality standards for $PM_{2.5}$ to an annual average of 15 μg/m^3 and daily average of 35 μg/m^3 came into effect from March 27, 2018. Fine dust forecasts are also being issued according to these strengthened air quality standards. Moreover, recognizing the seriousness of the $PM_{2.5}$ problem, the government announced comprehensive measures for fine dust on September 24, 2017 to supplement and reinforce the "Special Measures for the Management of Fine Dust" in 2016.

To establish an effective policy for reducing $PM_{2.5}$ concentrations, the chemical characteristics of $PM_{2.5}$ must be determined and their sources identified. In this study, we collected $PM_{2.5}$ samples over a long period from intensive air pollution monitoring supersites operated by the Korean Ministry of Environment, measured their $PM_{2.5}$ concentration and analyzed their elemental, ionic and carbonaceous components to examine the concentration profile and seasonal characteristics of $PM_{2.5}$, with the aim of providing data for reducing the $PM_{2.5}$ concentration in Korea on the basis of scientific research.

2. Methodology

2.1 Monitoring Sites

The Korean Ministry of Environment established an intensive air pollution monitoring program in 2007 to elucidate the physico-chemical characteristics of long-range transported and locally emitted aerosols. Although the National Institute of Environmental Research (NIER) actually operates and monitors six supersites (Baengnyeong, Seoul, Gwangju, Daejeon, Jeju and Ulsan) in Korea. As shown in Fig. 1, we conducted the present study at the Seoul supersite located in Bulgwang-dong, Eunpyeong-gu, Seoul (37°61'N, 126°93'E), the Daejeon supersite located in Munhwa-dong, Jung-gu, Daejeon (36°32'N, 127°41'E), the Gwangju supersite located in Oryong-dong, Buk-gu, Gwangju (35°23'N, 126°85'E), the Baengnyeong supersite (37°57'N, 124°53'E), the Jeju supersite (33°35'N, 126°39'E) and the Ulsan supersite located in Seongan-dong, Ulsan (35°58'N, 129°32'E). The Seoul supersite is located in the northwestern part of Seoul. Since it is a representative

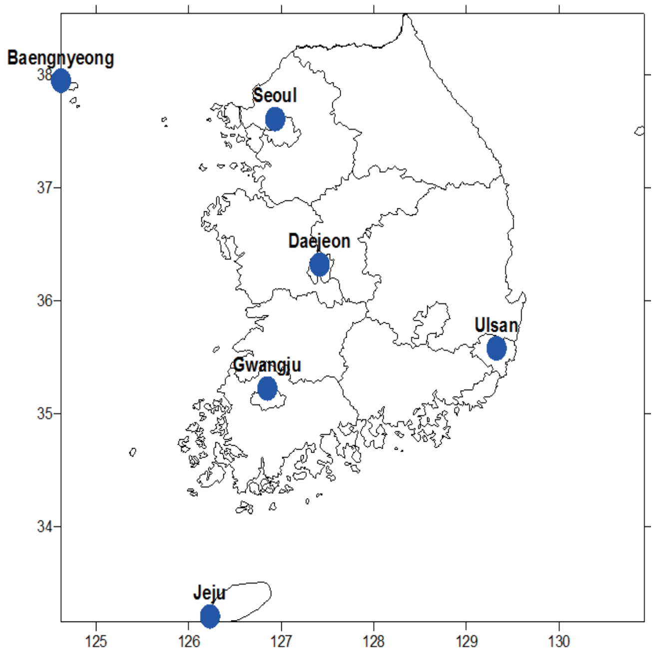

Fig. 1 Locations of the sampling sites.

urban area where residential and commercial buildings are concentrated and Mount Bukhan lies to its northeast, the Seoul supersite is a suitable monitoring location for determining the causes and characteristics of high-density air pollution cases that occur in cities and in the long-range transboundary to cities. The Daejeon supersite is adjacent to roadways, and thus it is a suitable location for determining the effects of traffic volume in downtown areas. Moreover, Daejeon is an area that can be affected by the coal-fired power plants in the Chungcheong-do region. As for the Gwangju supersite, it is a place that blends the characteristics of farmland and urban areas (Koo *et al.*, 2018). The Baengnyeong supersite is on Baengnyeong Island, located off the far western part of the Korean Peninsula in the Yellow Sea between China and Korea, approximately 200 km from China's Shandong Peninsula. Korea's NIER designed the Baengnyeong supersite to measure regional background concentrations from eastern China and the Seoul supersite to monitor local concentrations in Seoul. Under northwesterly wind conditions, the polluted air mass that originates in northern China is transported to Seoul via Baengnyeong Island. The supersites were designed to identify the effects of long-range transboundary pollution on air quality in Korea. (NIER, 2014a) The Jeju supersite is located on Mount Halla and is part of a background area that is not much affected by surrounding emission sources. The Ulsan supersite was established in Ulsan to identify the air quality characteristics of industrial areas, and it is possible to determine the air quality effects on industrial and residential areas according to changes in wind direction (Lyu *et al.*, 2015).

From January 1 through December 31, 2014, we collected $PM_{2.5}$ samples from 0 am to 0 am the next day every day for 24 hours a day using a low-volume air sampler (16.7 L/min) at the six supersites in Korea. Monitoring was suspended at the Jeju supersite from January to March, and at the Baengnyeong supersite in December due to equipment problems. Each sampler was equipped with WINS (Well Impactor Ninety-Six) for collecting $PM_{2.5}$ samples. The samples were collected using PT47DMC-KR (2.0 μm, 47 mm, MTL, LLC) filters made of PTFE (polytetrafluoroethylene) for analyzing $PM_{2.5}$ mass concentration and element content, Zefluor™ (2.0 μm, 47 mm, Pall Co.) filters for analyzing water-soluble ionic content, and quartz (Tissuquartz 2500 QAT-UP, 47 mm, Pall Co.) filters for analyzing carbonaceous content.

2.2 Measurement of $PM_{2.5}$ Mass Concentration

The US, Europe and Japan have adopted the gravimetric measurement method as the standard method for measuring $PM_{2.5}$ concentration, and the federal reference method (FRM) for measuring $PM_{2.5}$ in the US is based on 24-hour cumulative collection using filter paper. The EPA admits only measurement data using instruments and methods that adhere to its guidelines as $PM_{2.5}$ data, and the relevant guidelines are given in US EPA (1997) APPENDIX L TO PART 50 (NIER, 2014b). In this study we calculated the concentrations using the gravimetric measurement method, and for weighing mass concentrations we used an automated filter weighing system (Mettler Toledo UMX2, Ultra-microbalance) that maintains constant temperature (20℃) and humidity (35%). The collected filters were sealed and kept in thermostatic desiccators for storing filters at constant temperature and humidity. The filters were kept in a horizontal position and iceboxes were used to transport the samples. Weighing was conducted after the filters were kept at constant mass in the chamber for 24 hours, and the $PM_{2.5}$ concentrations were calculated by dividing the weight difference before and after sample collection by volume (NIER, 2013). To calibrate the $PM_{2.5}$ mass concentration, laboratory field blanks were used in the process of measuring the weight of each batch of filters, and after they were moved to the sample collection sites, they were collected without undergoing the sampling process and were weighed once again for the purpose of quality control.

2.3 Water-soluble Inorganic Ions

For the analysis of water-soluble ions, the filter was placed in an inert-material beaker with its sampled side facing down, then 200 μL of ethanol and 20 mL of de-ionized water with resistivity of at least 18 MΩ were added and stirred for 120 minutes to produce an extract. The extract was then strained through a filter (Toyo 5C) with a pore size of 0.1 μm and diameter of 110 mm, and component analysis (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) was conducted using ion chromatography (IC 2000, Thermo).

As for analysis conditions, in the case of anions we used an IonPac-AS15 separator column (3×150 mm, Thermo, USA), IonPac AG15 guard column (3×30 mm, Thermo, USA), ASRS-300, 2 mm anion micro-membrane suppressor and KOH gradient eluent. For cations we used an IonPac CS12 separator column (3×150 mm, Thermo, USA), IonPac CG12 guard column (3×30 mm, Thermo, USA), CSRS-300 suppressor (2 mm, Thermo, USA) and 18 mM MSA (methane sulphonic acid) eluent.

2.4 Carbonaceous Components

For analyzing organic carbon (OC) and elemental carbon (EC), we used quartz filters (Tissuquartz 2500 QAT-UP, PALL, USA) that were pretreated by heating at 650℃ for at least four hours. The filters used for collecting samples were sealed and kept in a frozen state to prevent the volatilization of their carbonaceous content and contamination of the filters. They were analyzed using the TOT (Thermal/Optical Transmittance) method for calculating OC and EC concentrations by measuring the CO_2 generated at different temperatures when burning the collected samples. We made holes of uniform size (1.0×1.5 cm) in the quartz fiber filters used to collect the samples, and analyzed them by means of a carbon analyzer (Lab OC/EC Analyzer, Sunset, USA). For the OC/EC analysis, a Thermal/Optical Carbon Aerosol Analyzer was employed, operating according to NIOSH Method 5040.

The analytical process was divided into two main stages. In the first stage, helium was used as a carrier gas to measure OC by sorting it into different sections according to temperature, namely, OC1 (-310℃), OC2 (-475℃), OC3 (-615℃), and OC4 (-870℃). In the second stage, the oven temperature was lowered, and oxygen was injected as an oxidizer to measure EC by sorting it into six components, namely, EC1 (-550℃), EC2 (-625℃), EC3 (-700℃), EC4 (-775℃), EC5 (-850℃), and EC6 (-870℃), under a catalytic reaction condition of 2% oxygen and 98% helium (Jeon *et al*., 2015).

2.5 Elemental Components

Elemental content was analyzed using ED-XRF (Energy Dispersive X-Ray Fluorescence analyzer, Epsilon5, PANalytical, Netherlands). The X-ray detector was germanium and the energy range, 0.7-100 keV. Liquid nitrogen (LN_2) was used for cooling. The X-ray tube was a Gd anode, side-window type, with voltage in the range of 25-100 kV and current of 0.5-24 mA (maximum power: 600 W). There were 27 elements targeted for analysis, namely, Si, K, Ca, Ti, Mn, Fe, Zn, Sc, V, Cr, Co, Ni, Cu, As, Se, Br, Rb, Sr, Mo, Cd, Sn, Sb, Te, Cs, Ba, Hg and Pb, and we used an aerosol membrane (Nucleipore) at three concentration levels for 36 elements as a reference. The relative standard deviation (RSD) was calculated to be within 10%, and the detection limit fell in the range of 0.2-5.9 ng/m^3. We used SRM 2783 (Serial No. 1345) from NIST (National Institute of Standard and Technology) to check for reproducibility and to improve the accuracy of our analysis.

3. Results and Discussion

3.1 Meteorological Characteristics

The national average annual temperature of the whole country in 2014 was 13.1℃. The annually averaged highest temperature was recorded as 18.6℃ and the lowest, 8.4℃. Annual mean precipitation was 1173.5 mm, amounting to 89.8% of a normal year, and the number of precipitation days was 111.9, which was 8.4 days more than a normal year. Comparing monitoring locations, Jeju Island had the highest mean temperature and Baengnyeong Island the lowest. The wind speed at Jeju and Baengnyeong islands was strong compared to the other regions. Baengnyeong Island had the lowest precipitation, and the precipitation in Seoul was 641.6 mm less than in a normal year, thus amounting to a total precipitation that was less than those of most other regions (KMA, 2014). The annual mean temperature (℃), wind speed (m/s), total precipitation (mm) and relative humidity (%) at the six sampling sites are presented in Table 1.

Figure 2 shows $PM_{2.5}$ concentrations according to incoming wind direction. In the case of Seoul, westerly and southwesterly were the dominant wind directions, and high concentrations occurred frequently when the wind came from the southwest. Much of Seoul's

Table 1 Meteorological characteristics.

Region*	Temperature	Wind speed	Precipitation	Relative humidity
SU	13.4℃	2.6 m/s	808.9 mm	63%
DJ	13.4℃	1.5 m/s	1117.7 mm	72%
GJ	14.3℃	1.9 m/s	1290.3 mm	65%
BN	11.6℃	4.2 m/s	391.9 mm	69%
JJ	16.2℃	3.2 m/s	1563.4 mm	70%
US	14.7℃	2.2 m/s	1398.7 mm	64%
National average	13.1℃	2.1 m/s	1173.5 mm	68%

* (SU: Seoul, DJ: Daejeon, GJ: Gwangju, BN: Baengnyeong, JJ: Jeju, US: Ulsan)
(Source: Korea Meteorological Administration, *Annual Climatological Report* (2014))

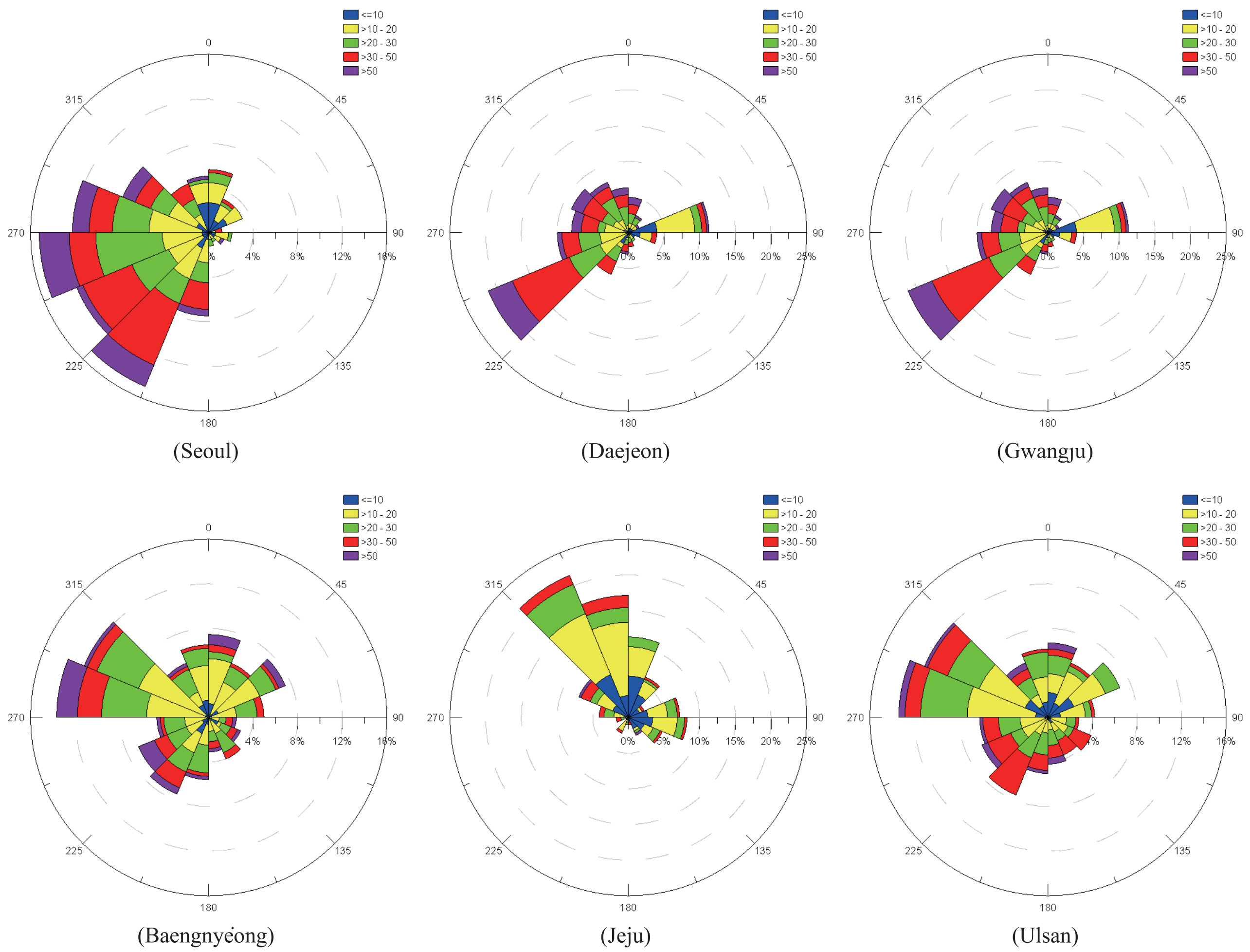

Fig. 2 Pollutant roses, by $PM_{2.5}$ concentration ($\mu g/m^3$).

industrial area is located in the southwestern part of the city. In a stable atmospheric state, the effect of local emissions seems to influence the concentration level of Seoul area.

Daejeon and Gwangju likewise showed high concentrations when the wind came from the southwesterly direction. Baengnyeong Island and Ulsan had high concentrations when the wind came from the northwest, thus showing a marked difference from Seoul and Daejeon. In particular, the high concentrations in the Baengnyeong islet area appeared mainly under northwesterly wind conditions, and it is thought that long-distance mobility contributes to domestic concentrations considerably when considering the geographical background characteristics of the domestic inflow.

3.2 $PM_{2.5}$ Mass Concentrations

During the sampling period, the $PM_{2.5}$ concentration range was 3.5–118.5 μg/m^3 in Seoul, 3.4–103.8 μg/m^3 in Daejeon, 3.6–104.3 μg/m^3 in Gwangju, 4.3–130.3 μg/m^3 in Baengnyeong, 3.0–51.5 μg/m^3 in Jeju and 4.4–97.7 μg/m^3 in Ulsan. The mean concentrations, as shown in Table 2, were 25.9 μg/m^3 in Seoul, 28.1 μg/m^3 in Daejeon, 27.4 μg/m^3 in Gwangju, 24.1 μg/m^3 in Baengnyeong, 15.5 μg/m^3 in Jeju and 22.4 μg/m^3 in Ulsan. Thus the urban areas of Daejeon and Gwangju showed high concentration levels, followed by Seoul, Baengnyeong, Ulsan and Jeju. In the case Gwangju, the mean concentration of 27.4 μg/m^3 in 2014 was a slight increase from that of the previous year (23.1 μg/m^3) (Sung *et al.*, 2017). The number of times $PM_{2.5}$ concentration exceeded the daily average of 35 μg/m^3, the current ambient air quality standard, was 60 times for Seoul, 58 for Daejeon, 66 for Gwangju, 28 for Baengnyeong, three for Jeju and 34 for Ulsan. Thus high concentration cases occurred relatively frequently in Seoul, Daejeon and Gwangju, while Baengnyeong and Jeju had low numbers of such cases compared to the other regions.

Table 2 Annual average of $PM_{2.5}$ mass concentration (μg/m^3).

	Mass		Mass
Seoul	25.9 ± 17.9	Baengnyeong	24.1 ± 17.1
Daejeon	28.1 ± 18.2	Jeju	15.5 ± 10.0
Gwangju	27.4 ± 17.3	Ulsan	22.4 ± 13.2

Figure 3 shows monthly $PM_{2.5}$ concentrations by region, which exhibited a tendency to be high in winter and low in summer and autumn. $PM_{2.5}$ concentrations in winter were the highest, at 37.1, 39.8 and 35.5 μg/m^3, respectively, in Seoul, Daejeon and Gwangju, whereas Baengnyeong, Jeju, and Ulsan, respectively, had high concentrations of 27.4, 16.3 and 25.1 μg/m^3 in spring. In summer, $PM_{2.5}$ concentrations were 18.9 μg/m^3 in Seoul, 19.5 μg/m^3 in Daejeon, 21.0 μg/m^3 in Gwangju, 22.6 μg/m^3 in Baengnyeong, 14.4 μg/m^3 in Jeju and 20.5 μg/m^3 in Ulsan; in autumn, 16.1 μg/m^3 in Seoul, 21.8 μg/m^3 in Daejeon, 19.9 μg/m^3 in Gwangju, 19.1 μg/m^3 in Baengnyeong, 12.1 μg/m^3 in Jeju and 17.4 μg/m^3 in Ulsan. Thus $PM_{2.5}$ concentrations in summer and autumn were lower than those in spring and winter. In Seoul, the mean $PM_{2.5}$ concentrations in spring (March–May), summer (June–August), autumn (September–November), and winter (December–February) were 33.7, 18.9, 16.1 and 37.1 μg/m^3, respectively; in Daejeon they were 31.1, 19.5, 21.8 and 39.8 μg/m^3, respectively; in Gwangju, 32.0, 21.0, 19.9 and 35.5 μg/m^3, respectively; in Baengnyeong, 27.8, 22.6, 19.1 and 27.4 μg/m^3, respectively; in Jeju, 19.3, 14.4, 12.1 and 16.3 μg/m^3 respectively; and in Ulsan, 26.5, 20.5, 17.4 and 25.1 μg/m^3, respectively. Thus the concentrations in winter were about 1.2–2.0 times higher than those in summer. High concentration levels in winter arise from pollution resulting from the increased use of heating, and low concentration levels in summer reflect the cleansing effect of frequent precipitation. Moreover, in regional terms, the Seoul, Daejeon and Gwangju regions showed comparatively high concentration levels due to an increase in mobile pollution sources in the Seoul region and emissions from industrial areas.

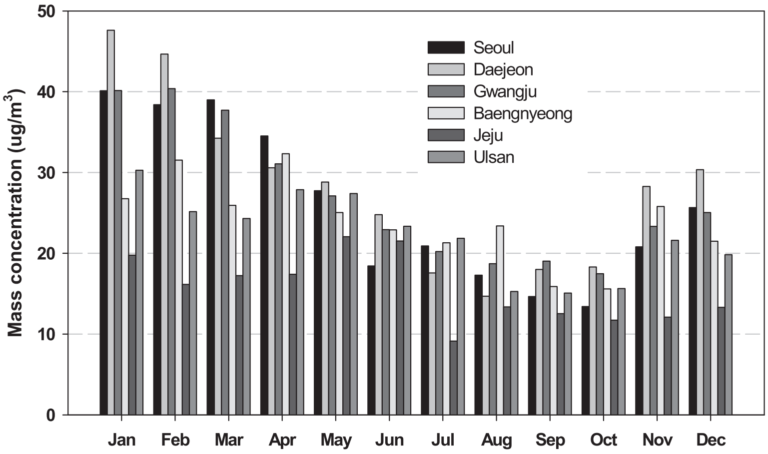

Fig. 3 Variability of the monthly mean concentrations for $PM_{2.5}$ at the six sites.

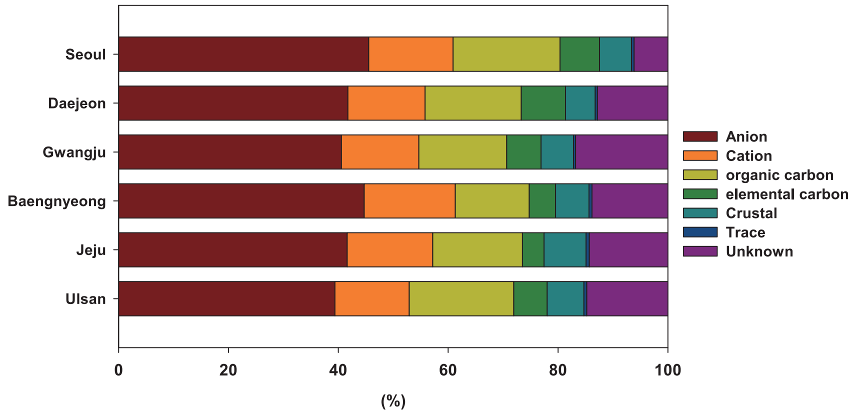

Fig. 4 Average compositional fractions (%) of $PM_{2.5}$ at the six sites.

Recently, the high $PM_{2.5}$ concentrations in the Korean Peninsula have mainly been caused by atmospheric congestion and high humidity. In other words, long-distance migration and domestic secondary production are the main causes of these high concentrations. Quantitative and qualitative estimations of these factors are known to be possible through chamber experiments and are not discussed in this study.

3.3 $PM_{2.5}$ Composition

The compositional ratios of $PM_{2.5}$ components as measured by this study are presented in Fig. 4. In Jeju and Ulsan, the ratios were in the order of anions > OC > cations > crustal matter > EC > trace elements. In the remaining three regions, excluding Baengnyeong, the ratios were in the order of anions > OC > cations > EC > crustal matter > trace elements. In the case of Baengnyeong Island, which serves as a background area for the Korean Peninsula, the ratio of OC and EC contents related to traffic volume and heating fuel were 13.5% and 4.8%, respectively, thus being low in comparison with Seoul (19.5% and 7.2%), Daejeon (17.5% and 8.1%), Gwangju (16.0% and 6.2%), and Ulsan (19.0% and 6.1%). As for the ratio of crustal matter, Jeju had 7.7%; Ulsan, 6.7%; and Baengnyeong, 6.1%, thus showing slightly higher ratios than Seoul at 5.8%, Daejeon at 5.4% and Gwangju at 5.9%. Seoul had the highest ratios of anion and carbonaceous content, and the Ulsan supersite situated by roadways had the highest EC ratio.

3.3.1 Water-soluble Ion Content Analysis Results

During the monitoring period, the anion concentrations in Seoul, Daejeon, Gwangju, Baengnyeong, Jeju and Ulsan were 11.7, 11.7, 11.1, 10.8, 6.4 and 8.8 μg/m^3, respectively, accounting for 39.4–45.5% of $PM_{2.5}$, while the cation concentrations were 4.0, 3.9, 3.9, 4.0, 2.4 and 3.0 μg/m^3, respectively, accounting for 13.5–16.6% of $PM_{2.5}$. It was found that Baengnyeong had the highest ratio of ionic content as compared to other regions. The ionic content analysis results for each region are as shown in Table 3, and in terms of components, anions appear in the order of SO_4^{2-} > NO_3^- > Cl^-, and cations in the order of NH_4^+ > Na^+ > K^+ > Ca^{2+} > Mg^{2+}. As for the secondary ionic components SO_4^{2-}, NO_3^- and NH_4^+, their concentrations accounted for the largest share of $PM_{2.5}$'s water-soluble ion content. This is similar to the findings of other studies (Jiang *et al*., 2018; Khan *et al*., 2010; Xu *et al*., 2017). Findings in Genoa, Italy (Salameh *et al*., 2015) showed ion content concentrations as low as in Jeju, Korea, and relatively high Ca^{2+} content was found in Thessaloniki, Greece (Tolis *et al*., 2015). In Yokohama, Japan (Khan *et al*., 2010), NO_3^- and SO_4^{2-} concentrations were found to be low compared to in Korea, whereas the Zhengzhou region in China (Jiang *et al*., 2018) showed higher concentrations not only in terms of mass but for all ionic components than at the six sites in Korea, and notably an extremely high concentration of SO_4^{2-}. Moreover, NO_3^- and SO_4^{2-} concentrations in the Handan and Xian regions of China (Xu *et al*., 2017) were also found to be very high.

3.4 Carbonaceous Content Analysis Results

Carbon particles are composed of organic carbon (OC) and elemental carbon (EC). OC is generated from various emission sources such as fossil fuel combustion, industrial processes and biological combustion. It consists of various kinds of organic matter mixed together, including polycyclic aromatic hydrocarbons (PAHs), which are harmful to the human body. EC is directly emitted from incomplete combustion, such as fossil fuel combustion and biomass burning, and contributes to global warming due to its non-volatile and light-absorbing properties (Tolis *et al*., 2015).

The mean OC concentrations in Seoul, Daejeon, Gwangju, Baengnyeong, Jeju and Ulsan were 5.02, 4.92, 4.38, 3.25, 2.53 and 4.27 μg/m^3 respectively, while the mean EC concentrations were 1.85, 2.27, 1.71, 1.15, 0.61 and 1.36 μg/m^3 respectively. As shown in Table 3, regional carbon component concentrations indicate OC appearing in the order of Seoul > Daejeon > Gwangju > Ulsan > Baengnyeong > Jeju, with Seoul and Daejeon (where the site is located by roadways) having the highest OC concentrations and Jeju the lowest. It seems that OC concentrations in the urban regions were higher

Table 3 Referential data on average concentrations of $PM_{2.5}$ mass, ion, carbon and elements at each site.

Region*		SU	DJ	GJ	BN	JJ	US	GE (Italy)	TH (Greece)	YO (Japan)	ZH (China)
Number	(ea)	231	200	212	145	75	202	184	149	91	150
$PM_{2.5}$ mass	(μg/m³)	25.8	28.1	27.4	24.1	15.5	22.4	14.0	37.7	20.58	144
Cl^-	(μg/m³)	0.19	0.32	0.47	0.35	0.10	0.15		0.39	0.21	
NO_3^-		4.25	4.54	3.82	3.30	0.79	2.98	0.5	2.40	0.96	17.4
SO_4^{2-}		7.31	6.88	6.83	7.12	5.56	5.70		3.96	3.80	23.9
Na^+		0.16	0.15	0.14	0.37	0.17	0.17	0.1	0.29	0.25	
NH_4^+		3.55	3.55	3.42	3.18	2.08	2.67	1.4	3.80	2.27	12.8
K^+		0.17	0.18	0.22	0.27	0.10	0.12		0.14	0.13	
Mg^{2+}		0.02	0.02	0.02	0.05	0.01	0.01		0.07	0.05	
Ca^{2+}		0.07	0.06	0.07	0.13	0.06	0.05		1.43	0.20	
OC	(μg/m³)	5.02	4.92	4.38	3.25	2.53	4.27	2.7	6.62	3.75	20.6
EC		1.85	2.27	1.71	1.15	0.61	1.36	1.4	1.29	1.94	6.8
Si	(ng/m³)	894.0	886.9	937.6	878.6	789.2	894.1				
K		325.4	330.2	361.9	358.9	209.0	237.6	100	418		
Ti		7.5	7.0	7.6	6.8	6.1	9.7		3		
Pb		23.7	26.2	25.4	26.1	12.5	21.9	6	45		247
Cd		2.8	2.4	2.8	2.2	2.4	2.9				7
Cu		6.7	5.6	4.9	4.0	2.9	5.3	6	170		33
Mn		11.0	11.4	14.4	9.4	6.1	22.7	4	91		76
Fe		139.6	159.9	163.6	113.8	89.8	193.3	142	864		1051
Ni		2.0	2.0	1.7	2.4	1.6	3.3	7	27		5
Zn		62.3	63.6	68.1	51.9	33.9	69.3	19	196		598
As		4.1	4.0	3.6	5.6	2.3	6.0				18
Ca		58.7	63.1	63.3	49.5	53.3	72.2	110	1921		

* (SU: Seoul, DJ: Daejeon, GJ: Gwangju, BN: Baengnyeong, JJ: Jeju, US: Ulsan, GE: Genoa; Salameh (2015), TH: Thessaloniki; Tolis (2015), YO: Yokohama; Khan (2010), ZH: Zhengzhou; Jiang (2018))

than those in the island regions due to the presence of more car emissions and residential areas in the former. As for EC, Daejeon had the highest concentration and Jeju the lowest. The Daejeon site, which is heavily affected by roadways, along with the Seoul region with its high traffic volume, had the highest EC concentrations indicating the impact of primary emissions, whereas Jeju Island with its comparative lack of primary emission sources had a lower EC concentration than the other locations. This result is in line with study findings by other researchers (Tolis *et al*., 2015). Research findings in Greece (Tolis *et al*., 2015) show that OC concentrations there were higher than at the six sites in Korea, while Yokohama (Khan *et al*., 2010) had lower OC concentrations than all the regions in Korea excluding Baengnyeong and Jeju. However, the Zhengzhou region in China (Jiang *et al*., 2018) had much higher concentrations of all the ionic components than the six sites in Korea.

3.5 Elemental Components

As for the mean concentrations of elements, major components of fugitive dust and crustal matter such as K, Ca and Fe, respectively, had high concentrations in Seoul (325.41, 58.47, and 139.61 ng/m³), Daejeon (330.24, 63.10, and 159.87 ng/m³), Gwangju (361.92, 63.32, and 163.6 ng/m³), Baengnyeong (358.87, 49.54, and 113.83 ng/m³), Jeju (209.01, 53.3, 89.77 ng/m³) and Ulsan (237.62, 72.22, 193.35 ng/m³). The 27 elements targeted for the $PM_{2.5}$ analysis, accounted for 6.3% of $PM_{2.5}$ in Seoul, with crustal elements (Si, K, Ca, Ti, Mn, Fe, and Zn) constituting 1.50 μg/m³ (5.8%), and trace elements constituting 0.13 μg/m³ (0.5%). In Daejeon, elements accounted for 5.8% of $PM_{2.5}$, with crustal elements constituting 1.52 μg/m³ (5.4%) and trace elements constituting 0.11 μg/m³ (0.4%). In Gwangju, they accounted for 6.3% of $PM_{2.5}$, with crustal elements constituting 1.62 μg/m³ (5.9%) and trace elements, 0.1 μg/m³ (0.4%) ; in Baengnyeong, 6.6% of $PM_{2.5}$, with crustal elements constituting 1.47 μg/m³ (6.1%), and trace elements, 0.13 μg/m³ (0.5%) ; in Jeju, 8.3% of $PM_{2.5}$, with crustal elements constituting 1.19 μg/m³ (7.7%) and trace elements, 0.09 μg/m³ (0.6%) ; in Ulsan, 7.2% of $PM_{2.5}$, with crustal elements constituting 1.50 μg/m³ (6.7%) and trace elements, 0.11 μg/m³ (0.5%). Jeju had a higher ratio of crustal elements than Daejeon, while Seoul and Gwangju exhibited similar levels of concentrations.

As for Fe, Zn and Pb, they were observed to have high concentrations in the order of Fe＞Zn＞Pb. Fe and Zn mainly derive from vehicle exhaust emissions (Sung *et al*., 2015), and tend to have high concentrations in Daejeon, Seoul and Gwangju where there is dense traffic. In regard to other specific elements, As had concentrations of 4.1 ng/m³ in Seoul, 4.0 ng/m³ in Daejeon, 3.6 ng/m³ in Gwangju, 5.6 ng/m³ in

Baengnyeong, 2.3 ng/m^3 in Jeju and 6.0 ng/m^3 in Ulsan, showing that Ulsan had the highest concentration. The source of As is thought to be waste incineration. Cd is known to be emitted at high temperatures from the burning of coal, petroleum and wastes (Sung *et al.*, 2015), and it had concentrations of 2.8 ng/m^3 in Seoul, 2.4 ng/m^3 in Daejeon, 2.8 ng/m^3 in Gwangju, 2.2 ng/m^3 in Baengnyeong, 2.4 ng/m^3 in Jeju and 2.9 ng/m^3 in Ulsan, exhibiting concentration levels that did not vary conspicuously across different regions. The Genoa region in Italy (Salameh *et al.*, 2015) had lower concentrations of most elements than Korea. excluding Ca, while Thessaloniki in Greece (Tolis *et al.*, 2015) and Zhengzhou in China (Jiang *et al.*, 2018) had much higher concentrations of all the elements than the six sites in Korea.

3.6 Seasonal Distribution

Table 4 shows the seasonal characteristics of each region. Due to equipment problems there was no monitoring at Jeju from January to March, or at Baengnyeong in December. As for $PM_{2.5}$ concentrations in winter, Seoul had 35.2 μg/m^3, Daejeon 41.7, μg/m^3; Gwangju, 38.2 μg/m^3; Baengnyeong, 29.4 μg/m^3; and Ulsan, 25.9 μg/m^3. For the most part, high concentrations were frequently found in winter when there is increased burning of fuels, and relatively low concentrations were found in summer and autumn when there is a lot of rainfall. Jeju, however, exhibited higher concentrations in spring and summer. In the case of ions, NH_4^+, NO_3^-, and SO_4^{2-} exhibited much variation according to season. The mean concentrations of NH_4^+ by season were distributed in the order of winter>spring>summer>autumn for all regions except Jeju, and those of NO_3^- were distributed in the order of winter>spring>autumn>summer for the regions excluding Baengnyeong and Jeju. SO_4^{2-} showed much variance in distribution for each region, and exhibited the lowest concentrations in autumn with the exception of in Jeju, which had the lowest concentration in winter. NO_3^- concentrations in Seoul, Daejeon, Gwangju, Baengnyeong and Ulsan were high in winter and low in summer. This is because most of the HNO_3 gases produced through the reaction of NO_2 exist in particulate form during winter, but mostly in a gaseous state during summer, with NO_3^- concentrations in particular being affected by NOx, the emission of which varies according to season (Xu *et al.*, 2017; Yu *et al.*, 2015). In spring, summer and autumn, SO_4^{2-} concentrations were higher than NO_3^- concentrations, but winter NO_3^- concentrations were higher than those of SO_4^{2-} in Seoul and Daejeon. The high nitrate concentration in Seoul and Daejeon is considered to be closely related to increased heating in winter and increased automobile traffic in Korea. This is similar to the study results of Xu *et al.* (2017).

As an external factor, it is thought that an increased heating capacity in northeastern China and increased long- range transportation due to winter westerlies have affected the complexity.

As for the seasonal characteristics of the elements,

Table 4 Seasonal variation of $PM_{2.5}$chemical components over the six sites (unit: μg/m^3).

		Mass	SO_4^{2-}	NO_3^-	NH_4^+	OC	EC	Crustal	Trace
SU	spring	33.2	9.1	5.9	4.5	5.9	1.8	2.05	0.10
	summer	19.0	8.0	1.2	3.0	4.4	1.5	1.07	0.07
	fall	14.8	4.3	2.4	2.1	3.8	1.7	1.18	0.05
	winter	35.2	6.4	8.3	4.4	6.1	2.7	1.79	0.11
DJ	spring	30.8	7.8	4.7	3.9	4.9	2.4	1.94	0.08
	summer	19.7	7.4	0.9	2.7	4.8	1.8	1.19	0.07
	fall	20.1	3.6	2.8	1.9	4.7	2.0	1.14	0.07
	winter	41.7	7.8	9.7	5.4	5.8	2.9	1.81	0.12
GJ	spring	33.6	7.6	3.8	3.3	5.2	2.0	2.15	0.10
	summer	22.0	7.9	0.8	2.9	3.9	1.0	1.45	0.07
	fall	20.4	3.9	2.4	2.0	4.6	1.4	1.25	0.06
	winter	38.2	8.6	8.6	5.8	5.5	2.8	1.89	0.10
BN	spring	29.4	8.7	5.2	4.1	3.2	1.5	1.60	0.10
	summer	23.4	7.7	1.7	3.0	2.9	0.7	1.30	0.09
	fall	20.1	4.6	1.6	2.0	3.8	1.1	1.59	0.07
	winter ※	29.4	9.1	4.8	4.3	4.1	1.6	1.79	0.09
JJ	spring ※	19.0	6.2	0.8	2.3	2.9	1.0	2.09	0.06
	summer	16.6	6.5	1.1	2.5	2.3	0.5	0.93	0.06
	fall	12.0	4.4	0.4	1.6	2.4	0.5	0.86	0.05
	winter ※	13.9	4.0	0.8	1.5	2.4	0.6	1.05	0.09
US	spring	25.8	6.7	3.8	3.2	4.9	1.6	2.15	0.09
	summer	20.4	5.8	1.9	2.4	4.8	1.4	1.21	0.09
	fall	17.9	4.1	1.8	1.9	3.6	0.9	1.31	0.07
	winter	25.9	6.1	4.3	3.1	3.9	1.5	1.62	0.08

※ No data for Baengnyeong in December, and for Jeju from January to March.

most regions showed high concentrations of crustal elements in spring due to the influence of Asian dust, with the next highest concentrations occurring in winter. EC consists mostly of primary pollutants that are directly released into the atmosphere from their emission sources through the use of fossil fuels, biomass burning, etc. (Lyu *et al*., 2015). EC concentrations were high in Seoul, Daejeon, Gwangju and Baengnyeong, which is in line with the results of Ren *et al*. (2017). Moreover, it was found that EC concentrations at the urban supersites were higher than those of background regions. OC concentrations were generally higher in winter than in summer, but in Ulsan they were high in spring and summer.

4. Conclusions

From January 1 through December 31, 2014, we collected $PM_{2.5}$ samples for 24 hours a day using low-volume air samplers at six supersites in Korea, and investigated the seasonal composition characteristics.

1. the $PM_{2.5}$ concentration range was 3.5–118.5 μg/m^3 in Seoul, 3.4–103.8 μg/m^3 in Daejeon, 3.6–104.3 μg/m^3 in Gwangju, 4.3–130.3 μg/m^3 in Baengnyeong, 3.0–51.5 μg/m^3 in Jeju and 4.4–97.7 μg/m^3 in Ulsan. The mean concentrations were 25.9 μg/m^3 in Seoul, 28.1 μg/m^3 in Daejeon, 27.4 μg/m^3 in Gwangju, 24.1 μg/m^3 in Baengnyeong, 15.5 μg/m^3 in Jeju and 22.4 μg/m^3 in Ulsan. Thus the urban areas of Daejeon and Gwangju showed high concentration levels.

2. Water-soluble inorganic ions accounted for 52.9% to 61.3% of the total $PM_{2.5}$ mass concentrations. Sulfate, nitrate and ammonium were the major water-soluble ions in the aerosol. The mean OC concentrations in Seoul, Daejeon, Gwangju, Baengnyeong, Jeju and Ulsan were 5.02, 4.92, 4.38, 3.25, 2.53, and 4.27 μg/m^3, respectively, while the mean EC concentrations were 1.85, 2.27, 1.71, 1.15, 0.61, and 1.36 μg/m^3, respectively. As for element components in $PM_{2.5}$, they accounted for 7.2, 8.2, 6.6, 6.3, 5.8 and 6.3% of $PM_{2.5}$ in Seoul, Daejeon, Gwangju, Baengyeong, Ulsan and Jeju, respectively.

3. As for $PM_{2.5}$ concentrations in winter, Seoul had 35.2 μg/m^3; Daejeon, 41.7 μg/m^3; Gwangju, 38.2 μg/m^3; Baengnyeong, 29.4 μg/m^3; and Ulsan 25.9 μg/m^3. For the most part, high concentrations were frequently found in winter when there is increased burning of fuels. Jeju exhibited higher concentrations in spring and summer. In the case of ions, NH_4^+, NO_3^-, and SO_4^{2-} exhibited much variation according to season. As for the seasonal characteristics of elements, most regions showed high concentrations of crustal elements in spring. Organic carbon concentrations were generally higher in winter than in summer.

This study presents data from six sites in Korea that were constantly monitored over the span of one year, and it should be possible to use them as reliable basic data on $PM_{2.5}$. We believe that they can be used to provide foundational information needed to establish effective measures for reducing $PM_{2.5}$.

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(Received 22 June 2018, Accepted 2 November 2018)