

# Ionic Compositions of PM<sub>10</sub> and PM<sub>2.5</sub> Related to Meteorological Conditions at the Gosan Site, Jeju Island from 2013 to 2015

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## ABSTRACT

PM<sub>10</sub> and PM<sub>2.5</sub> were collected at the Gosan Site on Jeju Island from 2013 to 2015, and their ionic and elemental species were analyzed to examine the variations in their chemical compositional characteristics related to different meteorological conditions. Concentrations of nss-SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> were respectively 6.5 and 4.7 times higher in the fine particle mode (PM<sub>2.5</sub>) compared to the coarse particle mode (PM<sub>10-2.5</sub>), however NO<sub>3</sub><sup>-</sup> concentrations were 2.4 times higher in the coarse mode compared to the fine particle mode. During Asian dust days, the concentrations of nss-Ca<sup>2+</sup> and NO<sub>3</sub><sup>-</sup> increased to 8.2 and 5.0 times higher in PM<sub>10</sub>, and 3.5 and 6.0 times higher in PM<sub>2.5</sub>, respectively. During haze days, the concentrations of secondary pollutants increased by 3.1-4.7 and 3.2-7.9 in PM<sub>10</sub> and PM<sub>2.5</sub>, respectively, and they were, respectively, 1.2-2.1 and 0.9-2.1 times higher on mist days. The aerosols were acidified largely by sulfuric and nitric acids, and neutralized mainly by ammonia in the fine particle mode during the haze days, but neutralized by calcium carbonate in coarse particle mode during the Asian dust days. Clustered back trajectory analysis showed that concentrations of nss-SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were relatively high when air masses travelled from China.

**Key words:** PM<sub>10</sub>, PM<sub>2.5</sub>, Coarse particle, Fine particle, Asian dust, Haze

## 1. INTRODUCTION

Korea is experiencing difficulties in air quality management due to the effects of transboundary pollutants transported from the Asian continent over a long distance (Han *et al.*, 2006). Most of the recent smog phenomena have been due to high concentrations of fine

particulate matter.

Atmospheric aerosols are particulate matter suspended in a solid and liquid state in the air. The shapes of these aerosol particles vary according to their source, particle size, and atmospheric environment, and have different chemical compositions. In addition, Asian dust, haze, and mist affect the composition of atmospheric aerosols. The distribution of organic carbon, water-soluble ion components, and harmful heavy metals is different according to the meteorological phenomena. Therefore, it is meaningful to compare and evaluate the chemical composition of atmospheric aerosols according to the weather phenomenon by distinguishing them by size (Lee *et al.*, 2014).

Generally, coarse particles (2.5 < D<sub>p</sub> < 10 μm) of atmospheric aerosols are generated by mechanical processes on the surface. Their atmospheric residence time is relatively short, once exposed to organisms, most are caught in upper respiratory organs, such as the mouth or nose. However, fine particles (D<sub>p</sub> < 2.5 μm) are produced by chemical processes, such as condensation and agglomeration of atmospheric materials (Hyeon *et al.*, 2014; McMurry *et al.*, 2004; Seinfeld *et al.*, 1998). They mainly contain large quantities of secondary products, such as NH<sub>3</sub>, SO<sub>2</sub>, and NO<sub>x</sub> emitted from industrial facilities. In particular, microparticles with dimension between 0.1 and 1.0 μm in diameter are highly hazardous because they are absorbed and transported with vaporized carbon, sulfuric acid, and heavy metals when inhaled into the human body, and penetrate into the lungs (Na and Lee, 2000). Furthermore, microparticles tend to stay in the atmosphere for long periods of time and are transported long distances, so local pollution can broaden to the surrounding area (Shin *et al.*, 1996).

In this study, we investigated the effects of various meteorological phenomena on the chemical composition of atmospheric aerosols. For this purpose, PM<sub>10</sub> and PM<sub>2.5</sub> were collected from the Gosan site on Jeju Island. Aerosols were analyzed to investigate pollutant

characteristics, and were compared with compositional changes affected by Asian dust, haze, and mist events. We also investigated the effects of long-range transported pollutants from the Asian continent on atmospheric aerosols.

## 2. EXPERIMENTAL

### 2.1 Sample Collection

PM<sub>10</sub> and PM<sub>2.5</sub> samples were collected at the Gosan background site (33°17'N, 126°10'E) on Jeju Island, Korea, from 2013 to 2015 using PM<sub>10</sub> and PM<sub>2.5</sub> sequential air samplers (APM Engineering, PMS-103 and PMS-104, Korea) with a teflon filter (Pall Co., Zefluor™, PTFE 47 μm, 2.0 μm, USA). Flow rates for the air samplers were maintained at 16.7 L/min using a mass flow controller. The collected sample filters were sealed in petri dishes (SPL life science, PS, 52.7 × 12.6 mm) onsite, and then dried in a desiccator until reaching a constant weight. Dried sample filters were stored in a freezer maintained at -24°C until analysis (Kim *et al.*, 2014). In total 315 sample filters were collected for PM<sub>10</sub> and 301 for PM<sub>2.5</sub>. The PM<sub>10</sub> and PM<sub>2.5</sub> sample filters were divided into four groups based on meteorological conditions: 15 and 14 for PM<sub>10</sub> and PM<sub>2.5</sub> during Asian dust days, 23 and 24 during haze days, and 116 and 115 during mist days, respectively. The total number of non-event samples were 161 and 148 for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively.

### 2.2 Analysis of Ionic Components

Water-soluble ionic components were extracted from the sample filters by adding 0.2 mL of ethanol and 30 mL of ultrapure water (18.2 MΩ·cm) and agitating them in an ultrasonic extractor for 30 min and shaker for 1 h (200 rpm). After filtering insoluble species from the extract using a syringe filter (Whatman, PVDF syringe filter, 0.45 μm), the filtrates were used for ionic component analysis.

The major water-soluble ionic species were analyzed by ion chromatography (Modula IC, equipped with a 907 IC pump and 732 IC detector, Metrohm, Herisau, Switzerland) using the Metrohm Metrosep Cation C6-150 column with 3.0 mM nitric acid eluent for cations, and the Metrosep A-SUPP-16 column with 7.5 mM Na<sub>2</sub>CO<sub>3</sub> eluent and 200 mM H<sub>2</sub>SO<sub>4</sub> suppressor solutions for anions.

Standard solutions for cation (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) analyses were prepared using 100 μg/mL AccuStandards, and diluted to various concentrations (0.1-5.0 μg/mL) to make the standard calibration curves. The standard calibration curve calculated from the standard solutions showed good linearity; the coefficient of determination (R<sup>2</sup>) was higher than 0.9999. The standard solutions for anion (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>) analyses were prepared using primary standard reagents (Sigma, 99.999% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 99.99% KNO<sub>3</sub>, and 99.99% NaCl). The standard calibration curve was calculated using standard solutions with concentrations of 0.1-5.0 μg/mL. The standard solutions for the analysis of trace organic acid ions (HCOO<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>), F<sup>-</sup>, and CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> were made using high purity reagents (Sigma, 99.99% NaF, 99.9% CH<sub>3</sub>COONa·3H<sub>2</sub>O, 99% HCOONa, and 98% CH<sub>3</sub>SO<sub>3</sub>Na), and diluted to concentrations of 0.01-0.5 μg/mL for calculating standard calibration curves. The correlation between the standard calibration curve and standards for analyzing anions and organic acids showed good linearity; the coefficients of determination were ≥ 0.9999.

Based on the seven repeated analyses by ion chromatography, the instrument detection limits (IDLs) for the IC analyses were in the range of 0.3-10.7 μg/mL for the twelve analyzed ionic species, and the coefficient of variation (CV) ranged from 0.1 to 3.3%.

## 3. RESULTS AND DISCUSSION

### 3.1 Mass Concentrations of Atmospheric Aerosols

The mass concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> during non-event days excluding Asian dust, haze, mist and heavy rainfall (over 3 mm), were 35.7 ± 15.3 μg/m<sup>3</sup> and 14.8 ± 8.5 μg/m<sup>3</sup>, respectively. The mass concentration observed using the β-ray absorption method by Korea Meteorological Administration, was 25.8 ± 11.2 μg/m<sup>3</sup>, which was somewhat lower than this study. The correlation coefficient between the two measurements was about r=0.75. In addition, Lee *et al.* (2015) also demonstrated a somewhat lower result than the PM<sub>2.5</sub> mass concentration, 18.6 μg/m<sup>3</sup> measured in 2008-2012 at the Gosan area. This value was also 1.6-1.8 times lower compared to the PM<sub>10</sub> mass concentrations; 57.8, 64.5, 61.2, and 59.4 μg/m<sup>3</sup>, respectively, measured in 2009 in the major metropolitan areas of Seoul, Gyeonggi, Incheon, and Busan (Table 1).

### 3.2 Water-soluble Ionic Concentrations

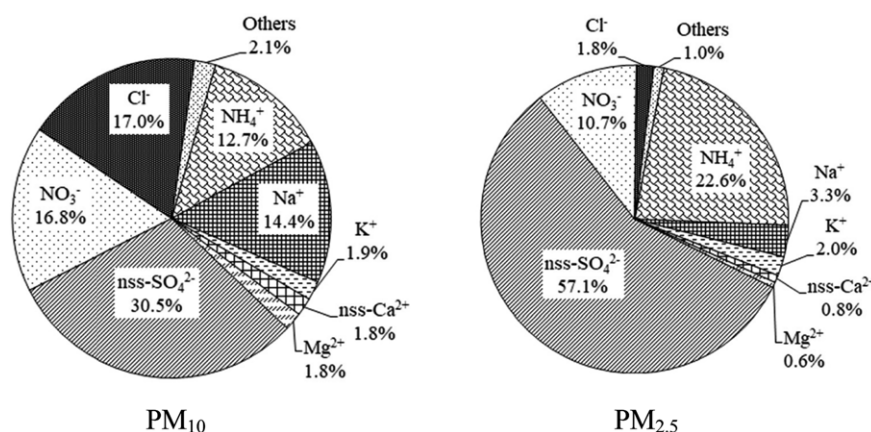
The ionic concentrations of PM<sub>10</sub> on the non-event days were in the order; nss-SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Na<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > K<sup>+</sup> > Mg<sup>2+</sup> > nss-Ca<sup>2+</sup> > CH<sub>3</sub>COO<sup>-</sup> > HCOO<sup>-</sup> > CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> > F<sup>-</sup>. The major secondary pollutants (nss-SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) accounted for 60.0% of total ionic composition, followed by the sea salt (Na<sup>+</sup>, Cl<sup>-</sup>, and Mg<sup>2+</sup>) at 34.2%, the organic acid (CH<sub>3</sub>COO<sup>-</sup> and HCOO<sup>-</sup>) at 2.0%, and the soil components (nss-Ca<sup>2+</sup>) at 1.8% (Table 2 and Fig. 1).

**Table 1.** Mass concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> at Gosan and other metropolitan sites.

Site	Concentration ( $\mu\text{g}/\text{m}^3$ )			Reference
	PM <sub>10</sub>	PM <sub>2.5</sub>	Period	
Gosan, Jeju	35.7 ± 15.3	14.8 ± 8.5	2013-2015	This study
Gosan, Jeju	—	18.6	2008-2012	Lee <i>et al.</i> , 2015
Seoul	57.8	—	2009	Lim <i>et al.</i> , 2012
Gyeonggi	64.5	—	2009	Lim <i>et al.</i> , 2012
Incheon	61.2	—	2009	Lim <i>et al.</i> , 2012
Busan	59.4	—	2009	Lim <i>et al.</i> , 2012

**Table 2.** Concentrations and relative abundances of water-soluble ionic species in PM<sub>10</sub> and PM<sub>2.5</sub> particles.

Species	Concentration ( $\mu\text{g}/\text{m}^3$ )			Ratio (PM <sub>10-2.5</sub> /PM <sub>2.5</sub> )
	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10-2.5</sub>	
NH <sub>4</sub> <sup>+</sup>	2.18 ± 1.31	1.80 ± 1.03	0.38	0.2
Na <sup>+</sup>	2.49 ± 1.74	0.27 ± 0.27	2.23	8.4
K <sup>+</sup>	0.33 ± 0.19	0.16 ± 0.12	0.17	1.1
nss-Ca <sup>2+</sup>	0.31 ± 0.21	0.06 ± 0.03	0.25	4.0
Mg <sup>2+</sup>	0.32 ± 0.19	0.05 ± 0.03	0.27	6.0
nss-SO <sub>4</sub> <sup>2-</sup>	5.26 ± 2.45	4.56 ± 2.47	0.70	0.2
NO <sub>3</sub> <sup>-</sup>	2.90 ± 2.02	0.85 ± 1.24	2.05	2.4
Cl <sup>-</sup>	3.09 ± 2.78	0.15 ± 0.17	2.95	20.2
F <sup>-</sup>	0.01 ± 0.01	0.001 ± 0.001	0.01	4.4
HCOO <sup>-</sup>	0.08 ± 0.07	0.03 ± 0.04	0.04	1.4
CH <sub>3</sub> COO <sup>-</sup>	0.27 ± 0.42	0.04 ± 0.06	0.23	6.0
CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	0.01 ± 0.04	0.01 ± 0.01	0.003	0.3

**Fig. 1.** Relative contributions of water-soluble ionic species to PM<sub>10</sub> and PM<sub>2.5</sub> particle compositions.

The ionic concentrations of PM<sub>2.5</sub> on non-event days were in the order; nss-SO<sub>4</sub><sup>2-</sup> > NH<sub>4</sub><sup>+</sup> > NO<sub>3</sub><sup>-</sup> > Na<sup>+</sup> > K<sup>+</sup> > Cl<sup>-</sup> > nss-Ca<sup>2+</sup> > Mg<sup>2+</sup> > CH<sub>3</sub>COO<sup>-</sup> > HCOO<sup>-</sup> > CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> > F<sup>-</sup>. Of these components, nss-SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup>, which are of anthropogenic origin, were as high as 4.56, 1.80, and 0.85  $\mu\text{g}/\text{m}^3$ , respectively. In contrast, Na<sup>+</sup>, Cl<sup>-</sup>, and nss-Ca<sup>2+</sup> components were relatively low in concentration. Secondary pollutants (nss-

SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) accounted for 90.4% of the total ion composition, accounting for 1.5 times more of the total than in PM<sub>10</sub>. Sea salt (Na<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>) accounted for 5.7%, organic acid (HCOO<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>) accounted for 0.9%, and the soil component (nss-Ca<sup>2+</sup>) accounted for 0.8% of the total, demonstrating low relative abundances.

Comparing the distributions of ion components in

**Table 3.** Concentrations of ionic species in PM<sub>10</sub> and PM<sub>2.5</sub> particles, and their relative abundances during different meteorological conditions.

Species	Concentrations ( $\mu\text{g}/\text{m}^3$ )								Ratio					
	PM <sub>10</sub>				PM <sub>2.5</sub>				PM <sub>10</sub>			PM <sub>2.5</sub>		
	AD	HZ	MT	NE	AD	HZ	MT	NE	AD/NE	HZ/NE	MT/NE	AD/NE	HZ/NE	MT/NE
NH <sub>4</sub> <sup>+</sup>	6.63	8.29	3.97	2.18	5.11	6.74	3.38	1.80	3.0	3.8	1.8	2.8	3.7	1.9
Na <sup>+</sup>	3.73	3.12	2.19	2.49	0.43	0.37	0.28	0.27	1.5	1.3	0.9	1.6	1.4	1.1
K <sup>+</sup>	0.77	0.88	0.32	0.33	0.55	0.58	0.18	0.16	2.3	2.6	1.0	3.4	3.6	1.1
nss-Ca <sup>2+</sup>	2.58	1.03	0.34	0.31	0.22	0.11	0.08	0.06	8.2	3.3	1.1	3.5	1.8	1.3
Mg <sup>2+</sup>	0.60	0.50	0.30	0.32	0.08	0.07	0.05	0.05	1.9	1.6	0.9	1.7	1.6	1.1
nss-SO <sub>4</sub> <sup>2-</sup>	15.56	16.16	10.95	5.26	12.32	14.41	9.64	4.56	3.0	3.1	2.1	2.7	3.2	2.1
NO <sub>3</sub> <sup>-</sup>	14.44	13.52	3.47	2.90	5.11	6.72	0.77	0.85	5.0	4.7	1.2	6.0	7.9	0.9
Cl <sup>-</sup>	4.93	4.40	2.07	3.09	0.23	0.16	0.14	0.15	1.6	1.4	0.7	1.5	1.1	0.9
F <sup>-</sup>	0.05	0.02	0.00 <sub>4</sub>	0.01	0.00 <sub>5</sub>	0.00 <sub>3</sub>	0.00 <sub>1</sub>	0.00 <sub>1</sub>	7.1	3.2	0.5	3.5	2.0	0.4
HCOO <sup>-</sup>	0.12	0.16	0.06	0.08	0.04	0.05	0.02	0.03	1.6	2.0	0.8	1.4	1.4	0.6
CH <sub>3</sub> COO <sup>-</sup>	0.30	0.42	0.34	0.27	0.03	0.03	0.02	0.04	1.1	1.6	1.3	0.9	0.7	0.5
CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	0.05	0.03	0.06	0.01	0.05	0.02	0.02	0.01	3.7	2.2	4.2	4.2	1.6	2.0

AD: Asian Dust, HZ: Haze, MT: Mist, NE: Non-Event

PM<sub>10-2.5</sub> and PM<sub>2.5</sub>, shown in Table 1, the concentration ratio of PM<sub>10-2.5</sub>/PM<sub>2.5</sub> is < 1 for NH<sub>4</sub><sup>+</sup> and nss-SO<sub>4</sub><sup>2-</sup>, indicating that they were more distributed in the fine particle mode. However, Na<sup>+</sup>, Cl<sup>-</sup>, nss-Ca<sup>2+</sup>, Mg<sup>2+</sup>, and NO<sub>3</sub><sup>-</sup> had higher abundances in the coarse particle mode, and K<sup>+</sup> was uniformly distributed in coarse and fine particles.

In atmospheric aerosols of urban areas, NO<sub>3</sub><sup>-</sup> concentration is usually higher than nss-SO<sub>4</sub><sup>2-</sup>. This higher abundance is from NO<sub>3</sub><sup>-</sup> generation related to energy use and the influence of mobile pollutants. In previous studies, the ratios of nss-SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> in PM<sub>2.5</sub> fine particles in the urban areas of Seoul, Chuncheon, Suwon, Gwangju, and Chungju were 1.06, 1.62, 1.54, 1.21 and 1.03, respectively (Kang *et al.*, 2015; Lee *et al.*, 2009; Jung and Han, 2008). In addition, the values were 1.99, 1.48, and 1.66 in the urban areas of New York, Beijing, and Shanghai, respectively (Wang *et al.*, 2006, 2005). In contrast, the nss-SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> ratios of Baekryongdo and Deokjeokdo, which are domestic background areas, were 3.34 and 3.57, respectively, much higher than in the cities (Lee *et al.*, 2010, 2002). The nss-SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> ratio in the mountainous site of Jeju Island showed a large value of 5.3 for the PM<sub>2.5</sub> fine particles, indicating that the effect of anthropogenic emission due to mobile pollution sources was relatively low.

### 3.3 Concentration Variation by Meteorological Conditions

#### 3.3.1 Ionic Concentrations

The ion concentrations in PM<sub>10</sub> and PM<sub>2.5</sub> were compared based on Asian dust, haze, mist, and non-event days (Table 3). The concentrations of nss-Ca<sup>2+</sup> during

Asian dust days were 2.58 and 0.22  $\mu\text{g}/\text{m}^3$  in PM<sub>10</sub> and PM<sub>2.5</sub>, respectively, showing 3.2 and 3.5 times higher than those for the non-event days. NO<sub>3</sub><sup>-</sup> concentrations were also 5.0 and 6.0 times higher in PM<sub>10</sub> and PM<sub>2.5</sub>, respectively. However, nss-SO<sub>4</sub><sup>2-</sup> concentrations were 15.56 and 12.32  $\mu\text{g}/\text{m}^3$  in PM<sub>10</sub> and PM<sub>2.5</sub>, respectively; these concentrations were 3.0 and 2.7 times higher than those on non-event days, respectively, but were smaller differences than those for nss-Ca<sup>2+</sup>. The relatively high nitrate and sulfate ion concentrations in PM<sub>10</sub> during Asian dust days were due to the chemical reactions of nitric acid and sulfuric acid with soil basic substances on the surfaces of the aerosols, converting them into salts, such as Ca(NO<sub>3</sub>)<sub>2</sub> and CaSO<sub>4</sub> (Rengarajan *et al.*, 2011; Shin *et al.*, 2005).

In addition, NH<sub>4</sub><sup>+</sup> increased 3.0 and 2.8 times in PM<sub>10</sub> and PM<sub>2.5</sub>, respectively, during Asian dust days compared to the non-event days. However, in general, the concentrations of NH<sub>4</sub><sup>+</sup> in these coarse particles were somewhat unusual, given the tendency of NH<sub>4</sub><sup>+</sup> to be distributed in fine particles below 1.0  $\mu\text{m}$  in diameter. NH<sub>3</sub> is known to quickly produce the sulfate salts because of its high reactivity with H<sub>2</sub>SO<sub>4</sub> in the atmosphere. In addition, reactions can be occurred with other strong acidic substances, such as HNO<sub>3</sub> and HCl (Zhuang and Huebert, 1996). It is known that ammonium salts, such as NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>HSO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, produced by those reaction could be migrated to coarse particles through physical process such as adherence and desorption (Szigeti *et al.*, 2013; Park *et al.*, 2010; Yeatman *et al.*, 2001). The increase of NH<sub>4</sub><sup>+</sup> concentration in coarse particles might be due to those reactions in this study.

During haze days, the concentrations of anthropo-

genic species such as  $\text{NH}_4^+$ ,  $\text{nss-SO}_4^{2-}$ , and  $\text{NO}_3^-$ , increased by 3.1-4.7 times in PM<sub>10</sub> and 3.2-7.9 times in PM<sub>2.5</sub> compared with non-event days. These components showed higher increase than the other components, and especially  $\text{NO}_3^-$  concentration showed remarkable increase in the fine particles.

In the case of PM<sub>10</sub> and PM<sub>2.5</sub>, the concentrations of  $\text{NH}_4^+$  and  $\text{nss-SO}_4^{2-}$  were 1.8-2.1 times higher during mist days than during non-event days. This higher abundance is presumably due to meteorological factors, such as humidity and temperature, which affected the particle conversion into particulate matter and particle agglomeration, and furthermore contributed to the increase in particulate matter concentration (Lee *et al.*, 2013). In addition, the concentrations of these components were 1.2-8.7 times higher in haze days in comparison to mist days. In particular,  $\text{NO}_3^-$  concentrations during haze days were notably increased for PM<sub>2.5</sub> compared to PM<sub>10</sub>. However, the concentration of  $\text{CH}_3\text{SO}_3^-$  was relatively higher for mist days.

The ionic compositions on Asian dust, haze, mist, and non-event days were compared based on particle size (Figs. 2, 3). As shown, the major secondary pol-

lutants ( $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ ) accounted for 73.6%, 78.3%, and 76.4% of the PM<sub>10</sub> during Asian dusts, haze days, and mist days, respectively; at PM<sub>2.5</sub>, the composition ratios were much higher at 93.3%, 95.2%, and 94.5%, respectively. Notably, the ionic compositions of  $\text{NH}_4^+$  in PM<sub>2.5</sub> were similar, at 23.0% and 23.2%, respectively, for haze and mist days, on the other hand, the compositions of  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{2-}$  in haze days were higher than those in mist days. These suggested that the secondary ionic pollutants play an important role in forming haze. The greater enhancements of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  were probably ascribed to fast conversion of their precursors via multiphase reactions during haze days (Zhang *et al.*, 2016). In contrast,  $\text{nss-Ca}^{2+}$  accounted for 5.2% of PM<sub>10</sub> during Asian dust days, 2.4 and 3.7 times higher than during haze and mist days, respectively. Sea salt components, such as  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{Mg}^{2+}$ , showed high concentrations during mist day in both PM<sub>10</sub> and PM<sub>2.5</sub>.

### 3.4 Acidification and Neutralization Characteristics

Atmospheric sulfur and nitrogen oxides are convert-

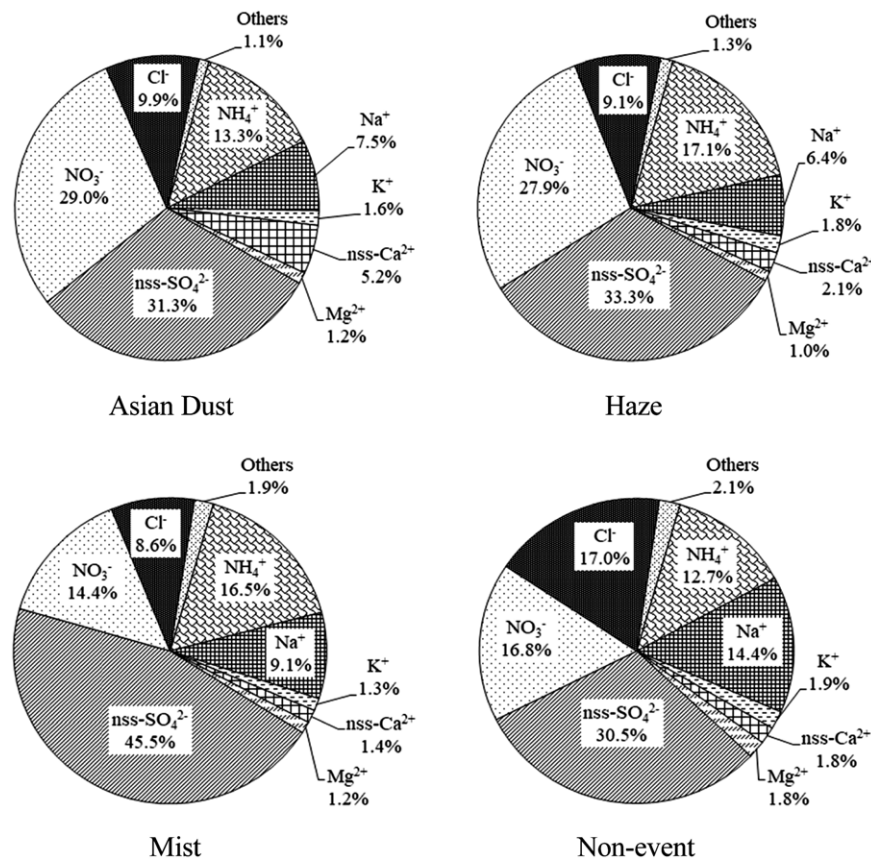


Fig. 2. Relative contributions of ionic species in PM<sub>10</sub> particles during Asian dust, haze, mist, and non-event days.

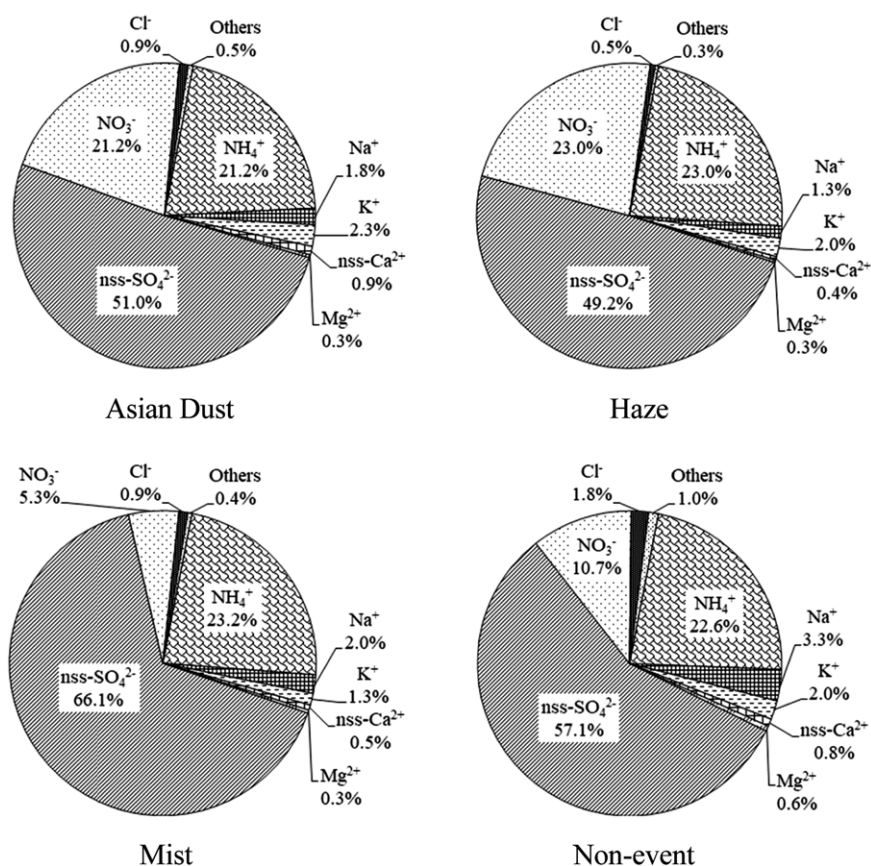


Fig. 3. Relative contributions of ionic species in PM<sub>2.5</sub> particles during Asian dust, haze, mist, and non-event days.

ed to sulfuric acid and nitric acid by photochemical oxidation; they are also present in aerosols in the form of sulfate or nitrate by neutralizing reactions with ammonia or a soil basic substance. Trace amounts of organic acids are also neutralized by ammonia and calcium carbonate (Seinfeld and Pandis, 1998). The acidification contribution from sulfuric acid and nitric acid was evaluated from equivalent concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, and compared by meteorological phenomena (Table 4). As shown in the table, the sum of cationic and anionic equivalent concentrations in PM<sub>10</sub> and PM<sub>2.5</sub> were similar on non-event and event days, suggesting that inorganic acids, such as sulfuric and nitric acids, significantly contributed to aerosol acidification. Furthermore, the sums of the cationic and anionic equivalent concentrations were high during Asian dust and haze days compared to non-event days. However, the sums of the cationic and anionic equivalent concentrations for mist days were relatively lower than those of Asian dust and haze days.

Ammonia and calcium carbonate are the primary contributors to the neutralization of acidic substances.

The degree of neutralization by these two substances can be evaluated by determining the neutralization factor (NF) through the following equations (1) and (2) (Galloway and Keene, 1989)

$$NF_{NH_4^+} = \frac{[NH_4^+]}{[nss-SO_4^{2-}] + [NO_3^-] + [HCOO^-] + [CH_3COO^-]} \quad (1)$$

$$NF_{nss-Ca^{2+}} = \frac{[nss-Ca^{2+}]}{[nss-SO_4^{2-}] + [NO_3^-] + [HCOO^-] + [CH_3COO^-]} \quad (2)$$

where [nss-SO<sub>4</sub><sup>2-</sup>], [NO<sub>3</sub><sup>-</sup>], [HCOO<sup>-</sup>], [CH<sub>3</sub>COO<sup>-</sup>], [NH<sub>4</sub><sup>+</sup>], and [nss-Ca<sup>2+</sup>] are each component's equivalent concentration. As shown in Table 5, the neutralization factors for ammonia on non-event days were 0.74 and 0.91 for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively; the degree of neutralization by ammonia was higher for fine particles. However, the neutralization factors for calcium carbonate were 0.10 and 0.03 for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively, indicating that it had a large influence on coarse particles. During Asian dust days, the

**Table 4.** Comparison between the sums of equivalent concentrations of basic cations and acidic anions in PM<sub>10</sub> and PM<sub>2.5</sub> particles.

Meteorology	PM <sub>10</sub> , µg/m <sup>3</sup>				PM <sub>2.5</sub> , µg/m <sup>3</sup>			
	Cation		Anion		Cation		Anion	
Non-event	H <sup>+</sup>	0.009	nss-SO <sub>4</sub> <sup>2-</sup>	0.109	H <sup>+</sup>	0.005	nss-SO <sub>4</sub> <sup>2-</sup>	0.095
	NH <sub>4</sub> <sup>+</sup>	0.121	NO <sub>3</sub> <sup>-</sup>	0.047	NH <sub>4</sub> <sup>+</sup>	0.100	NO <sub>3</sub> <sup>-</sup>	0.014
	nss-Ca <sup>2+</sup>	0.021	HCOO <sup>-</sup>	0.002	nss-Ca <sup>2+</sup>	0.003	HCOO <sup>-</sup>	0.001
	nss-Mg <sup>2+</sup>	0.001	CH <sub>3</sub> COO <sup>-</sup>	0.005	nss-Mg <sup>2+</sup>	0.001	CH <sub>3</sub> COO <sup>-</sup>	0.001
	Total	0.152	Total	0.163	Total	0.109	Total	0.111
Asian dust	H <sup>+</sup>	0.008	nss-SO <sub>4</sub> <sup>2-</sup>	0.324	H <sup>+</sup>	0.006	nss-SO <sub>4</sub> <sup>2-</sup>	0.256
	NH <sub>4</sub> <sup>+</sup>	0.368	NO <sub>3</sub> <sup>-</sup>	0.233	NH <sub>4</sub> <sup>+</sup>	0.283	NO <sub>3</sub> <sup>-</sup>	0.082
	nss-Ca <sup>2+</sup>	0.129	HCOO <sup>-</sup>	0.003	nss-Ca <sup>2+</sup>	0.011	HCOO <sup>-</sup>	0.001
	nss-Mg <sup>2+</sup>	0.012	CH <sub>3</sub> COO <sup>-</sup>	0.005	nss-Mg <sup>2+</sup>	0.002	CH <sub>3</sub> COO <sup>-</sup>	0.000 <sub>1</sub>
	Total	0.517	Total	0.565	Total	0.302	Total	0.339
Haze	H <sup>+</sup>	0.009	nss-SO <sub>4</sub> <sup>2-</sup>	0.336	H <sup>+</sup>	0.006	nss-SO <sub>4</sub> <sup>2-</sup>	0.300
	NH <sub>4</sub> <sup>+</sup>	0.459	NO <sub>3</sub> <sup>-</sup>	0.218	NH <sub>4</sub> <sup>+</sup>	0.374	NO <sub>3</sub> <sup>-</sup>	0.108
	nss-Ca <sup>2+</sup>	0.052	HCOO <sup>-</sup>	0.003	nss-Ca <sup>2+</sup>	0.006	HCOO <sup>-</sup>	0.001
	nss-Mg <sup>2+</sup>	0.010	CH <sub>3</sub> COO <sup>-</sup>	0.007	nss-Mg <sup>2+</sup>	0.002	CH <sub>3</sub> COO <sup>-</sup>	0.000 <sub>5</sub>
	Total	0.530	Total	0.564	Total	0.388	Total	0.410
Mist	H <sup>+</sup>	0.008	nss-SO <sub>4</sub> <sup>2-</sup>	0.239	H <sup>+</sup>	0.005	nss-SO <sub>4</sub> <sup>2-</sup>	0.202
	NH <sub>4</sub> <sup>+</sup>	0.220	NO <sub>3</sub> <sup>-</sup>	0.056	NH <sub>4</sub> <sup>+</sup>	0.187	NO <sub>3</sub> <sup>-</sup>	0.012
	nss-Ca <sup>2+</sup>	0.017	HCOO <sup>-</sup>	0.001	nss-Ca <sup>2+</sup>	0.004	HCOO <sup>-</sup>	0.000 <sub>4</sub>
	nss-Mg <sup>2+</sup>	0.003	CH <sub>3</sub> COO <sup>-</sup>	0.006	nss-Mg <sup>2+</sup>	0.001	CH <sub>3</sub> COO <sup>-</sup>	0.000 <sub>4</sub>
	Total	0.248	Total	0.302	Total	0.197	Total	0.215

neutralization factors for ammonia were 0.65 and 0.83 for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively. The neutralization factors for calcium carbonate were 0.23 and 0.03, respectively, demonstrating that the degree of neutralization by calcium carbonate was much higher in the coarse particles. However, during haze days, the neutralization factor for ammonia was 0.91 for PM<sub>2.5</sub>, which was higher than other event days. In addition, the neutralization factor for ammonia was 0.88 during mist days.

Based on the neutralization factors, it was found that the acidic substances in fine particles were mainly neutralized by ammonia, but the neutralization in coarse particles was occurred by calcium carbonate. In particular, the degree of neutralization by calcium carbonate was higher during Asian days in PM<sub>10</sub> particles, and the degree of neutralization by ammonia during haze days were much higher in PM<sub>2.5</sub>.

### 3.5 Influences of Air Mass Transport Pathways

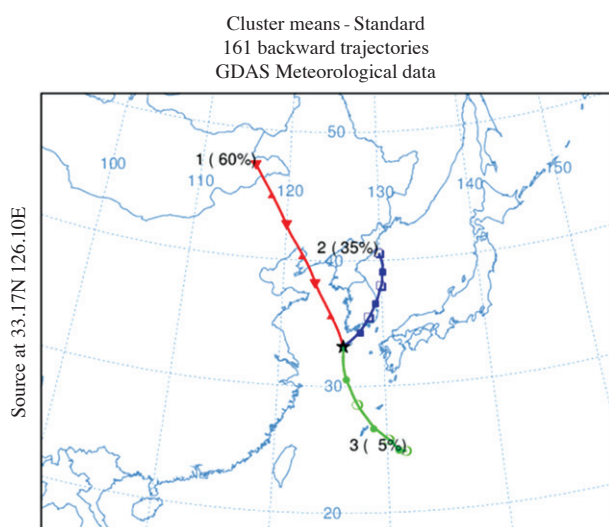
Based on the sampling days (161 days), the cluster back-trajectory analysis was performed in order to investigate the transport pathways of air masses using NOAA's HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model and GDAS meteorological

**Table 5.** Neutralization factors (NF) by ammonia and calcium carbonate in PM<sub>10</sub> and PM<sub>2.5</sub> particles for different meteorological conditions.

Meteorology	NF <sub>NH<sub>3</sub></sub>		NF <sub>CaCO<sub>3</sub></sub>	
	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10</sub>	PM <sub>2.5</sub>
Non-event	0.74	0.91	0.10	0.03
Asian Dust	0.65	0.83	0.23	0.03
Haze	0.81	0.91	0.09	0.01
Mist	0.76	0.88	0.06	0.02

data provided by the National Centers for Environmental Prediction (NCEP) (Draxler and Rolph, 2013; Kim *et al.*, 2004). The back-trajectory analysis was created for 72 hours based on 00 UTC for the corresponding sampling date. The altitude of the starting point for this cluster back-trajectory analysis was set at 72 m above sea level for Gosan site (Fig. 4).

As shown by the results of the cluster back-trajectory analysis, the pathways of air masses transported to the Gosan site were initially classified into three different categories: Cluster 1 (China continent), Cluster 2 (Korean Peninsula), and Cluster 3 (North Pacific). As shown in the figure, the frequency distribution of all transport pathways during the entire study period was



**Fig. 4.** Cluster back-trajectories for air masses corresponding to sampling dates at the Gosan Site.

60% (97 days), 35% (56 days), and 5% (8 days) for Clusters 1, 2, and 3, respectively, with inflow pathways from China continent accounting for the largest fraction. Comparing the concentrations of major ionic components by transport pathways of air masses,  $\text{NH}_4^+$ ,  $\text{nss-SO}_4^{2-}$ , and  $\text{NO}_3^-$  were highest, at 2.27, 5.36, and  $3.24 \mu\text{g}/\text{m}^3$ , respectively, when the air mass moved from China continent (Cluster 1) (Table 6). The concentration of soil-originated  $\text{nss-Ca}^{2+}$  was also high when the air masses were moving in from mainland China. In contrast, marine components, such as  $\text{Na}^+$  and  $\text{Cl}^-$ , were relatively higher when air masses were moving in from the North Pacific (Cluster 3).

#### 4. CONCLUSION

$\text{PM}_{10}$  and  $\text{PM}_{2.5}$  aerosols were collected from Korean background site and their water-soluble ionic components were analyzed. The results indicated that major anthropogenic components, such as  $\text{nss-SO}_4^{2-}$  and  $\text{NH}_4^+$ , were much higher in fine particles ( $\text{PM}_{2.5}$ ) than in coarse particles ( $\text{PM}_{10-2.5}$ ). However,  $\text{NO}_3^-$  was relatively higher in coarse particles. In  $\text{PM}_{10}$ , the major secondary pollutants ( $\text{nss-SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ ) accounted for 60.0% of the water-soluble ion components. In comparison, in  $\text{PM}_{2.5}$ , secondary pollutants accounted for 90.4% of the total, showing a much higher contribution in the fine particles.

During Asian dust days, the concentrations of  $\text{nss-Ca}^{2+}$  were higher in  $\text{PM}_{10}$ , while those of  $\text{nss-SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  were higher in  $\text{PM}_{2.5}$ . The concentra-

**Table 6.** Comparison of  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{nss-Ca}^{2+}$  concentration ( $\mu\text{g}/\text{m}^3$ ) in  $\text{PM}_{10}$  particles using cluster back-trajectory.

Pathway	$\text{nss-SO}_4^{2-}$	$\text{NO}_3^-$	$\text{NH}_4^+$	$\text{nss-Ca}^{2+}$
Cluster 1	5.36	3.24	2.27	0.37
Cluster 2	5.19	2.49	2.13	0.23
Cluster 3	4.53	1.78	1.54	0.21

tion of  $\text{nss-SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  increased in  $\text{PM}_{2.5}$  during haze days and concentrations of  $\text{NH}_4^+$  and  $\text{nss-SO}_4^{2-}$  in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were higher on mist days than on non-event days. Atmospheric aerosols at Gosan site were characterized by the influence of soil particles in  $\text{PM}_{10}$  during Asian dust events, and the effects of secondary pollutants were clear in  $\text{PM}_{2.5}$  during haze and mist days.

The acidification of atmospheric aerosols was mainly affected by sulfuric and nitric acids, and the neutralization of these inorganic acids was mainly caused by ammonia in  $\text{PM}_{2.5}$  and calcium carbonate in  $\text{PM}_{10}$ . In particular, during Asian dust days, the degree of neutralization by calcium carbonate was high in  $\text{PM}_{10}$ , while during haze days, the degree of neutralization by ammonia was high in  $\text{PM}_{2.5}$ .

Cluster back-trajectory analysis indicated that the concentration of major secondary pollutants and soil-originated components was higher when air masses moved from mainland of China, which is presumed to be severely affected by the air pollutants emitted from China.

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