

Ionic Compositions of PM₁₀ and PM_{2.5} Related to Meteorological Conditions at the Gosan Site, Jeju Island from 2013 to 2015

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ABSTRACT

PM₁₀ and PM_{2.5} 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-SO₄²⁻ and NH₄⁺ were respectively 6.5 and 4.7 times higher in the fine particle mode (PM_{2.5}) compared to the coarse particle mode (PM_{10-2.5}), however NO₃⁻ concentrations were 2.4 times higher in the coarse mode compared to the fine particle mode. During Asian dust days, the concentrations of nss-Ca²⁺ and NO₃⁻ increased to 8.2 and 5.0 times higher in PM₁₀, and 3.5 and 6.0 times higher in PM_{2.5}, respectively. During haze days, the concentrations of secondary pollutants increased by 3.1-4.7 and 3.2-7.9 in PM₁₀ and PM_{2.5}, 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-SO₄²⁻, NO₃⁻, and NH₄⁺ were relatively high when air masses travelled from China.

Key words: PM₁₀, PM_{2.5}, 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_p < 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_p < 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 NH₃, SO₂, and NO_x 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, PM₁₀ and PM_{2.5} 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

PM₁₀ and PM_{2.5} samples were collected at the Gosan background site (33°17'N, 126°10'E) on Jeju Island, Korea, from 2013 to 2015 using PM₁₀ and PM_{2.5} 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 PM₁₀ and 301 for PM_{2.5}. The PM₁₀ and PM_{2.5} sample filters were divided into four groups based on meteorological conditions: 15 and 14 for PM₁₀ and PM_{2.5} 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 PM₁₀ and PM_{2.5}, 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 Na₂CO₃ eluent and 200 mM H₂SO₄ suppressor solutions for anions.

Standard solutions for cation (NH₄⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺) 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 (R²) was higher than 0.9999. The standard solutions for anion (SO₄²⁻, NO₃⁻, and Cl⁻) analyses were prepared using primary standard reagents (Sigma, 99.999% (NH₄)₂SO₄, 99.99% KNO₃, 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⁻, CH₃COO⁻), F⁻, and CH₃SO₃⁻ were made using high purity reagents (Sigma, 99.99% NaF, 99.9% CH₃COONa·3H₂O, 99% HCOONa, and 98% CH₃SO₃Na), 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 PM₁₀ and PM_{2.5} during non-event days excluding Asian dust, haze, mist and heavy rainfall (over 3 mm), were 35.7 ± 15.3 μg/m³ and 14.8 ± 8.5 μg/m³, respectively. The mass concentration observed using the β-ray absorption method by Korea Meteorological Administration, was 25.8 ± 11.2 μg/m³, 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_{2.5} mass concentration, 18.6 μg/m³ measured in 2008-2012 at the Gosan area. This value was also 1.6-1.8 times lower compared to the PM₁₀ mass concentrations; 57.8, 64.5, 61.2, and 59.4 μg/m³, respectively, measured in 2009 in the major metropolitan areas of Seoul, Gyeonggi, Incheon, and Busan (Table 1).

3.2 Water-soluble Ionic Concentrations

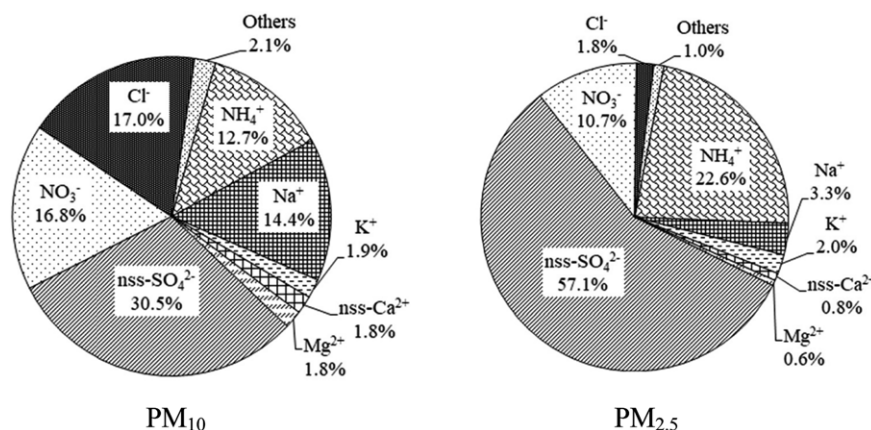
The ionic concentrations of PM₁₀ on the non-event days were in the order; nss-SO₄²⁻ > Cl⁻ > NO₃⁻ > Na⁺ > NH₄⁺ > K⁺ > Mg²⁺ > nss-Ca²⁺ > CH₃COO⁻ > HCOO⁻ > CH₃SO₃⁻ > F⁻. The major secondary pollutants (nss-SO₄²⁻, NO₃⁻, and NH₄⁺) accounted for 60.0% of total ionic composition, followed by the sea salt (Na⁺, Cl⁻, and Mg²⁺) at 34.2%, the organic acid (CH₃COO⁻ and HCOO⁻) at 2.0%, and the soil components (nss-Ca²⁺) at 1.8% (Table 2 and Fig. 1).

Table 1. Mass concentrations of PM₁₀ and PM_{2.5} at Gosan and other metropolitan sites.

Site	Concentration ($\mu\text{g}/\text{m}^3$)			Reference
	PM ₁₀	PM _{2.5}	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 PM₁₀ and PM_{2.5} particles.

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

**Fig. 1.** Relative contributions of water-soluble ionic species to PM₁₀ and PM_{2.5} particle compositions.

The ionic concentrations of PM_{2.5} on non-event days were in the order; nss-SO₄²⁻ > NH₄⁺ > NO₃⁻ > Na⁺ > K⁺ > Cl⁻ > nss-Ca²⁺ > Mg²⁺ > CH₃COO⁻ > HCOO⁻ > CH₃SO₃⁻ > F⁻. Of these components, nss-SO₄²⁻, NH₄⁺, and NO₃⁻, 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⁺, Cl⁻, and nss-Ca²⁺ components were relatively low in concentration. Secondary pollutants (nss-

SO₄²⁻, NO₃⁻, and NH₄⁺) accounted for 90.4% of the total ion composition, accounting for 1.5 times more of the total than in PM₁₀. Sea salt (Na⁺, Cl⁻, Mg²⁺) accounted for 5.7%, organic acid (HCOO⁻, CH₃COO⁻) accounted for 0.9%, and the soil component (nss-Ca²⁺) 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 PM₁₀ and PM_{2.5} particles, and their relative abundances during different meteorological conditions.

Species	Concentrations ($\mu\text{g}/\text{m}^3$)								Ratio					
	PM ₁₀				PM _{2.5}				PM ₁₀			PM _{2.5}		
	AD	HZ	MT	NE	AD	HZ	MT	NE	AD/NE	HZ/NE	MT/NE	AD/NE	HZ/NE	MT/NE
NH ₄ ⁺	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 ⁺	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 ⁺	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 ²⁺	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 ²⁺	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 ₄ ²⁻	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 ₃ ⁻	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 ⁻	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 ⁻	0.05	0.02	0.00 ₄	0.01	0.00 ₅	0.00 ₃	0.00 ₁	0.00 ₁	7.1	3.2	0.5	3.5	2.0	0.4
HCOO ⁻	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 ₃ COO ⁻	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 ₃ SO ₃ ⁻	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_{10-2.5} and PM_{2.5}, shown in Table 1, the concentration ratio of PM_{10-2.5}/PM_{2.5} is < 1 for NH₄⁺ and nss-SO₄²⁻, indicating that they were more distributed in the fine particle mode. However, Na⁺, Cl⁻, nss-Ca²⁺, Mg²⁺, and NO₃⁻ had higher abundances in the coarse particle mode, and K⁺ was uniformly distributed in coarse and fine particles.

In atmospheric aerosols of urban areas, NO₃⁻ concentration is usually higher than nss-SO₄²⁻. This higher abundance is from NO₃⁻ generation related to energy use and the influence of mobile pollutants. In previous studies, the ratios of nss-SO₄²⁻/NO₃⁻ in PM_{2.5} 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-SO₄²⁻/NO₃⁻ 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-SO₄²⁻/NO₃⁻ ratio in the mountainous site of Jeju Island showed a large value of 5.3 for the PM_{2.5} 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 PM₁₀ and PM_{2.5} were compared based on Asian dust, haze, mist, and non-event days (Table 3). The concentrations of nss-Ca²⁺ during

Asian dust days were 2.58 and 0.22 $\mu\text{g}/\text{m}^3$ in PM₁₀ and PM_{2.5}, respectively, showing 3.2 and 3.5 times higher than those for the non-event days. NO₃⁻ concentrations were also 5.0 and 6.0 times higher in PM₁₀ and PM_{2.5}, respectively. However, nss-SO₄²⁻ concentrations were 15.56 and 12.32 $\mu\text{g}/\text{m}^3$ in PM₁₀ and PM_{2.5}, 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-Ca²⁺. The relatively high nitrate and sulfate ion concentrations in PM₁₀ 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(NO₃)₂ and CaSO₄ (Rengarajan *et al.*, 2011; Shin *et al.*, 2005).

In addition, NH₄⁺ increased 3.0 and 2.8 times in PM₁₀ and PM_{2.5}, respectively, during Asian dust days compared to the non-event days. However, in general, the concentrations of NH₄⁺ in these coarse particles were somewhat unusual, given the tendency of NH₄⁺ to be distributed in fine particles below 1.0 μm in diameter. NH₃ is known to quickly produce the sulfate salts because of its high reactivity with H₂SO₄ in the atmosphere. In addition, reactions can be occurred with other strong acidic substances, such as HNO₃ and HCl (Zhuang and Huebert, 1996). It is known that ammonium salts, such as NH₄NO₃, NH₄HSO₄, and (NH₄)₂SO₄, 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 NH₄⁺ concentration in coarse particles might be due to those reactions in this study.

During haze days, the concentrations of anthropo-

genic species such as NH_4^+ , nss-SO_4^{2-} , and NO_3^- , increased by 3.1-4.7 times in PM₁₀ and 3.2-7.9 times in PM_{2.5} compared with non-event days. These components showed higher increase than the other components, and especially NO_3^- concentration showed remarkable increase in the fine particles.

In the case of PM₁₀ and PM_{2.5}, the concentrations of NH_4^+ and 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, NO_3^- concentrations during haze days were notably increased for PM_{2.5} compared to PM₁₀. However, the concentration of CH_3SO_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 (nss-SO_4^{2-} , NO_3^- , and NH_4^+) accounted for 73.6%, 78.3%, and 76.4% of the PM₁₀ during Asian dusts, haze days, and mist days, respectively; at PM_{2.5}, the composition ratios were much higher at 93.3%, 95.2%, and 94.5%, respectively. Notably, the ionic compositions of NH_4^+ in PM_{2.5} were similar, at 23.0% and 23.2%, respectively, for haze and mist days, on the other hand, the compositions of NO_3^- and 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 SO_4^{2-} , NO_3^- , and NH_4^+ were probably ascribed to fast conversion of their precursors via multiphase reactions during haze days (Zhang *et al.*, 2016). In contrast, nss-Ca^{2+} accounted for 5.2% of PM₁₀ during Asian dust days, 2.4 and 3.7 times higher than during haze and mist days, respectively. Sea salt components, such as Na^+ , Cl^- , and Mg^{2+} , showed high concentrations during mist day in both PM₁₀ and PM_{2.5}.

3.4 Acidification and Neutralization Characteristics

Atmospheric sulfur and nitrogen oxides are convert-

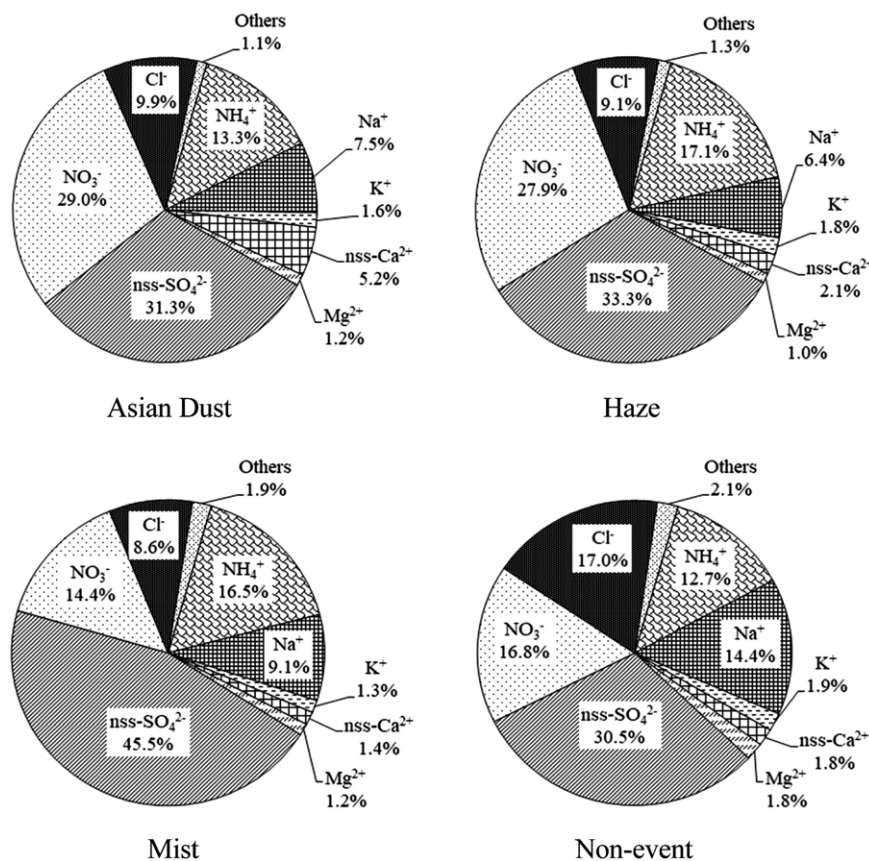


Fig. 2. Relative contributions of ionic species in PM₁₀ particles during Asian dust, haze, mist, and non-event days.

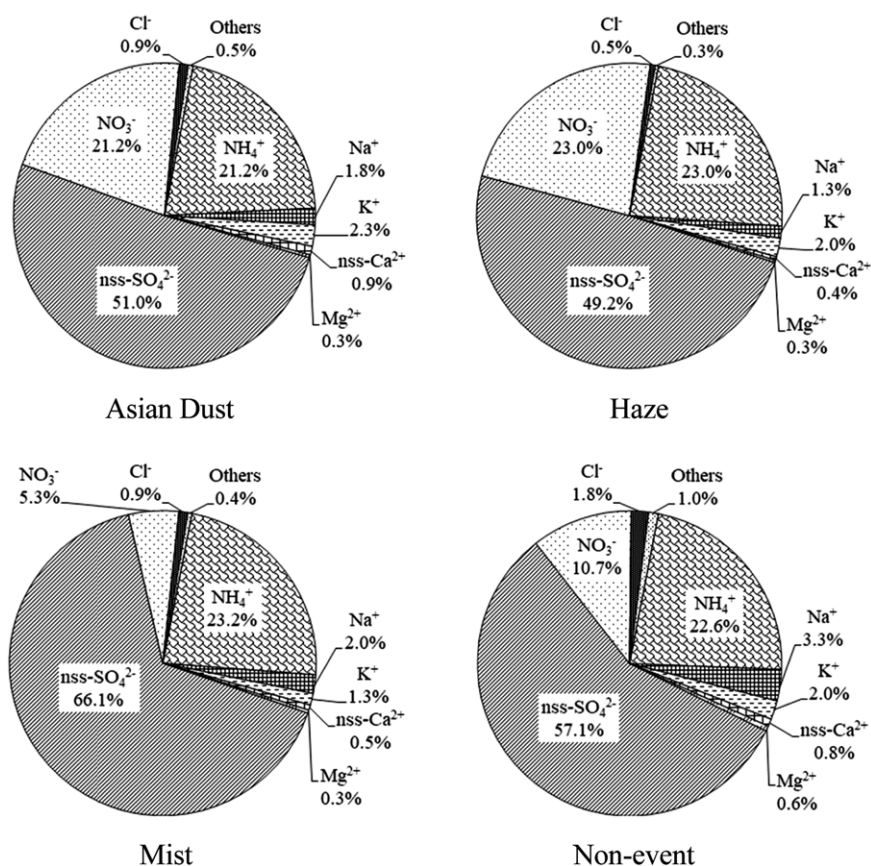


Fig. 3. Relative contributions of ionic species in PM_{2.5} particles during Asian dust, haze, mist, and non-event days.

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 SO₄²⁻ and NO₃⁻, and compared by meteorological phenomena (Table 4). As shown in the table, the sum of cationic and anionic equivalent concentrations in PM₁₀ and PM_{2.5} 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-SO₄²⁻], [NO₃⁻], [HCOO⁻], [CH₃COO⁻], [NH₄⁺], and [nss-Ca²⁺] 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 PM₁₀ and PM_{2.5}, 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 PM₁₀ and PM_{2.5}, 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 PM₁₀ and PM_{2.5} particles.

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

neutralization factors for ammonia were 0.65 and 0.83 for PM₁₀ and PM_{2.5}, 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_{2.5}, 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 PM₁₀ particles, and the degree of neutralization by ammonia during haze days were much higher in PM_{2.5}.

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 PM₁₀ and PM_{2.5} particles for different meteorological conditions.

Meteorology	NF _{NH₃}		NF _{CaCO₃}	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
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

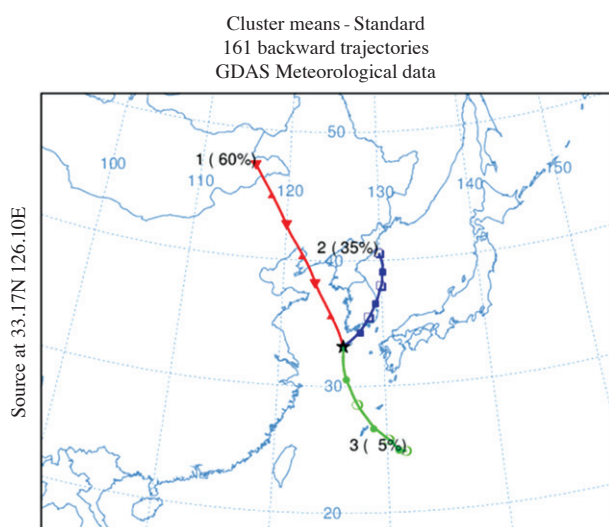


Fig. 4. Cluster back-trajectories for air masses corresponding to sampling dates at the Gosan Site.

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, NH_4^+ , nss-SO_4^{2-} , and 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 nss-Ca^{2+} was also high when the air masses were moving in from mainland China. In contrast, marine components, such as Na^+ and Cl^- , were relatively higher when air masses were moving in from the North Pacific (Cluster 3).

4. CONCLUSION

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 nss-SO_4^{2-} and NH_4^+ , were much higher in fine particles ($\text{PM}_{2.5}$) than in coarse particles ($\text{PM}_{10-2.5}$). However, NO_3^- was relatively higher in coarse particles. In PM_{10} , the major secondary pollutants (nss-SO_4^{2-} , NH_4^+ , and 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 nss-Ca^{2+} were higher in PM_{10} , while those of nss-SO_4^{2-} , NH_4^+ , and NO_3^- were higher in $\text{PM}_{2.5}$. The concentra-

Table 6. Comparison of nss-SO_4^{2-} , NO_3^- , NH_4^+ , and nss-Ca^{2+} concentration ($\mu\text{g}/\text{m}^3$) in PM_{10} particles using cluster back-trajectory.

Pathway	nss-SO_4^{2-}	NO_3^-	NH_4^+	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 nss-SO_4^{2-} , NH_4^+ , and NO_3^- increased in $\text{PM}_{2.5}$ during haze days and concentrations of NH_4^+ and nss-SO_4^{2-} in 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 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 PM_{10} . In particular, during Asian dust days, the degree of neutralization by calcium carbonate was high in 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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REFERENCES

- Draxler, R.R., Rolph, G.D. (2013) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT_traj.php).
- Galloway, J.N., Keene, W.C. (1989) Processes controlling the concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , H^+ , HCOO^- and CH_3COO^- in precipitation on Bermuda. *Tellus* 41B, 427-443.
- Han, J.S., Kim, Y.M., Ahn, J.Y., Kong, B.J., Choi, J.S., Lee, S.U., Lee, S.J. (2006) Spatial Distribution and Variation of Long-range Transboundary Air Pollutants Flux during 1997-2004. *Journal of Korean Society*

- Atmospheric Environment 22, 99-106.
- Hyeon, D.R., Song, J.M., Kim, K.J., Kim, W.H., Kang, C.H., Ko, H.J. (2014) Compositions of haze aerosols and their variation by inflow pathway of air mass at Gosan site in Jeju Island during 2012-2013. *Analytical Science & Technology* 27, 213-222.
- Jung, J.H., Han, Y.J. (2008) Study on Characteristics of PM_{2.5} and Its Ionic Constituents in Chuncheon, Korea. *Journal of Korean Society Atmospheric Environment* 24, 682-692.
- Kim, K.J., Lee, S.H., Hyeon, D.R., Ko, H.J., Kim, W.H., Kang, C.H. (2014) Composition comparison of PM₁₀ and PM_{2.5} fine particulate matter for Asian dust and haze events of 2010-2011 at Gosan site in Jeju Island. *Analytical Science & Technology* 27, 1-10.
- Kim, N.K., Kim, Y.P., Kang, C.H., Moon, K.C. (2004) Characteristics of Nitrate Concentration Measured at Gosan: Measurement Data of PM_{2.5} and TSP between 1998 and 2002. *Journal of Korean Society Atmospheric Environment* 20, 119-128.
- Kim, S., Lee, S. (2013) The Analysis of the Weather Characteristics by Source Region of the Asian Dust Observed in South Korea, *Journal of the Korean Geographical Society* 48, 167-183.
- Lee, D., Park, J., Kong, B., Lee, S., Kim, H., Park, J., Jeon, H., Seo, S. (2010) The Characteristics of the Air Pollutants Distribution and Concentration at the Baengnyeong Island(III). *National Institute of Environmental Research*. No. 2010-60-1235, 21.
- Lee, H.D., Lee, G.H., Kim, I.D., Kang, J.S., Oh, K.J. (2013) The Influences of Concentration Distribution and Movement of Air Pollutants by Sea Breeze and Mist around Onsan Industrial Complex. *Clean Technology* 19, 95-104.
- Lee, K.Y., Kim, Y.J., Kang, C.H., Kim, J.S., Chang, L.S., Park, K.H. (2015) Chemical characteristics of long-range-transported PM_{2.5} at Gosan, Jeju Island, in the spring and fall of 2008, 2009, 2011, and 2012. *Journal of Air & Waste Management Association* 65, 445-454.
- Lee, S.B., Bae, G.N., Kim, Y.P., Jin, H.C., Yoon, Y.S., Moon, K.C. (2002) Aerosol Characteristics at Tokchok Island in the Yellow Sea. *Journal of Korean Society Atmospheric Environment* 18, 305-316.
- Lee, Y.J., Jung, S.A., Jo, M.R., Kim, S.J., Park, M.K., Ahn, J.Y., Lyu, Y.S., Choi, W.J., Hong, Y.D., Han, J.S., Lim, J.H. (2014) Characteristics of PM Chemical Component during Haze Episode and Asian Dust at Gwang-ju. *Journal of Korean Society Atmospheric Environment* 30, 434-448.
- Lim, D., Lee, T.J., Kim, D.S. (2012) Quantitative Estimation of Precipitation Scavenging and Wind Dispersion Contributions for PM₁₀ and NO₂ Using Long-term Air and Weather Monitoring Database during 2000-2009 in Korea. *Journal of Korean Society Atmospheric Environment* 28, 325-347.
- McMurry, P., Shepherd, M., Vickery, J. (2004) Particulate Matter Science for Policy Makers; a NARSTO Assessment (Chapter 3), Cambridge University Press, U.K.
- Na, D.J., Lee, B.K. (2000) A Study on the Characteristics of PM₁₀ and Air-borne Metallic Elements Produced in the Industrial City. *Journal of Korean Society Atmospheric Environment* 16, 23-35.
- Park, J.S., Kim, C.H., Lee, J.J., Kim, J.H., Hwang, U.H., Kim, S.D. (2010) A Study on The Chemical Mass Composition of Particle Matter in Seoul. *Journal of Korean Society of Urban Environment* 10, 293-303.
- Rengarajan, R., Sudheer, A.K., Sarin, M.M. (2011) Wintertime PM_{2.5} and PM₁₀ carbonaceous and inorganic constituents from urban site in western India. *Atmospheric Research* 102, 420-431.
- Seinfeld, J.H., Pandis S.N. (1998) *Atmospheric Chemistry and Physics*, John Wiley & Sons, New York, U.S.A., 408.
- Shin, H.J., Lee, T.J., Kim, D.S. (1996) A Study on the Size Distribution of Trace Metals Concentrations in the Ambient Aerosols. *Journal of Korean Society Atmospheric Environment* 12, 67-77.
- Shin, S.A., Han, J.S., Hong, Y.D., Ahn, J.Y., Moon, K.J., Lee, S.J., Kim, S.D. (2005) Chemical Composition and Features of Asian Dust Observed in Korea (2000-2002). *Journal of Korean Society Atmospheric Environment* 21, 119-129.
- Szigeti, T., Mihucz, V.G., Óvári, M., Baysal, A., Atulgan, S., Akman, S., Záray, G. (2013) Chemical characterization of PM_{2.5} fractions of urban aerosol collected in Budapest and Istanbul. *Microchemical Journal* 107, 86-94.
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sun, Y., Chen, S., Zheng A. (2005) The ion chemistry and the source of PM_{2.5} aerosol in Beijing. *Atmospheric Environment* 39, 3771-3784.
- Wang, Y., Zhuang, G., Zhang, X., Huang, K., Xu, C., Tang, A., Chen, J., An, Z. (2006) The ion chemistry, seasonal cycle, and source of PM_{2.5} and TSP aerosol in Shanghai. *Atmospheric Environment* 40, 2935-2952.
- Yeatman, S.G., Spokes, L.J., Jickells, T.D. (2001) Comparisons of coarse-mode aerosol nitrate and ammonium at two polluted coastal sites. *Atmospheric Environment* 35, 1321-1335.
- Zhuang, L., Huebert, B.J. (1996) Lagrangian analysis of the total ammonia budget during Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange. *Journal Geophysical Research* 101, 4341-4350.
- Zhang, Y., Huang, W., Cai, T., Fanga, D., Wang, Y., Song, J., Hu, M., Zhang, Y. (2016) Concentrations and chemical compositions of fine particles (PM_{2.5}) during haze and non-haze days in Beijing. *Atmospheric Research* 174-175, 62-69.

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