

Seasonal Composition Characteristics of TSP and PM_{2.5} Aerosols at Gosan Site of Jeju Island, Korea during 2008-2011

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ABSTRACT

The collection of TSP and PM_{2.5} aerosols has been made at the Gosan Site of Jeju Island during 2008-2011, and their ionic and elemental species were analyzed, in order to examine the seasonal variation and characteristics of aerosol compositions. The anthropogenic components (NH₄⁺, nss-SO₄²⁻, NO₃⁻, S, Zn, Pb) and the soil components (nss-Ca²⁺, Al, Fe, Ca) showed high concentrations in spring as the prevailing westerly wind, but the concentrations of the sea-salt components (Na⁺, Cl⁻) were high in winter. In TSP, the neutralization by NH₃ increased in summer, but the neutralization by CaCO₃ increased in spring and fall seasons. The organic acids (HCOO⁻, CH₃COO⁻) contributed to the acidification of the aerosols by only 5.0%, so the acidification could be mostly contributed by the inorganic acids (SO₄²⁻, NO₃⁻). From the examination of the source origins by factor analysis, the compositions of TSP were influenced by the order of soil>anthropogenic>marine, on the other hand, those of PM_{2.5} were by the order of anthropogenic>marine>soil. The backward trajectory analyses showed that the concentrations of NH₄⁺, nss-SO₄²⁻, NO₃⁻ and nss-Ca²⁺ increased highly when the air masses had moved from China continent into Gosan area of Jeju Island.

Key words: TSP, PM_{2.5}, Gosan Site, Neutralization, Backward trajectory

1. INTRODUCTION

Due to a rapid industrial development as well as an expanding dissemination of the Asian dust, the amount of atmospheric pollutants has been increasingly produced in the Northeast Asia year by year. Especially, due to a long-range transport of atmospheric pollutants, the falling amounts of various acidic substances have

increased in Korea and Japan which are geographically located at a near distance from the coastal industry area of northeastern China and situated downwind by the prevailing westerly (Takami *et al.*, 2007; Arndt *et al.*, 1998; Kim *et al.*, 1996). For a reasonable air quality control, it is necessary to regulate the pollution emission and to secure the quantitative data for long-range transport and deposition of atmospheric pollutants. In this manner, a project (Long-range Transboundary Air Pollutants in Northeast Asia) has been performed cooperatively with Korea, China and Japan from 1997.

Jeju Island, one of the most unpolluted areas in Korea, is a vantage place for monitoring the long-range transported air pollutants from the continent of northeast Asia, since it is separated about 500 km away to the northeast from Shanghai of China and 100 km away to the south from the Korean peninsula. And the Gosan Site, located at the far western point of the Jeju Island, has been well known as a suitable monitoring place for background atmospheric aerosols due to almost no pollution sources nearby. Therefore, many researches for long-range transboundary air pollutants such as PEM-West A, PEM-West B, and APARE (East Asian/North Pacific Regional Experiment) by IGAC (International Global Atmospheric Chemistry) have been performed at the Gosan Site. Additionally, the ACE (Aerosol Characterization Experiment)-Asia project has been conducted to evaluate the influence on radiative forcing and climate change by atmospheric aerosols (Moon *et al.*, 2006; Huebert *et al.*, 2003; Carmichael *et al.*, 1997; Hoell *et al.*, 1996).

In this study, the compositions of atmospheric aerosols at the background area and their polluting characteristics have been investigated. The ionic and elemental components in TSP and PM_{2.5} aerosols collected at the Gosan Site during 2008-2011 have been analyzed, and the seasonal characteristics of chemical compositions as well as the acidity and neutralization contributions have been compared. The composition

variations by air mass inflow pathways and the emission sources of the aerosols have been also studied.

2. EXPERIMENTAL

2.1 Collection of Atmospheric Aerosols

The collection of TSP and PM_{2.5} aerosol samples was made at the Gosan Site (33° 17'N, 126° 10'E), which is located on the seashore hill of 72 m above sea level at the western edge of Jeju Island. The total 507 TSP samples (141 in 2008, 136 in 2009, 112 in 2010, 118 in 2011) have been collected using high volume tape sampler (KIMOTO Electric Co., 195A, Japan), which is an automatic system with roll type PTFE filters (Sumitomo Electric Co., 100 mm × 10 m) at 24 hour basis with every 3 day intervals from January of 2008 to December of 2011. On collecting samples, the air flow rate was kept to about 170 L/min, and total air flow was calculated from the flow rate and running time. Also, the PM_{2.5} aerosol samples have been collected for the total 468 (58 in 2008, 227 in 2009, 90 in 2010, 93 in 2011) using PM_{2.5} sequential air sampler (APM Engineering, PMS-103, Korea) with PTFE filters (Pall Co., Zeflour™, 47 mm, 2.0 μm) at 24 hour basis with every 3 day intervals for four years. The air flow rate was kept continuously to 16.7 L/min using automatic MFC system.

2.2 Chemical Analysis of the Aerosols

2.2.1 Ion Analysis

The collected TSP filters were moisturized with 0.2 mL of ethanol and extracted with 50 mL of ultrapure water by ultrasonication for 30 minutes and shaking for an hour. Similarly, the extraction procedure was performed with 30 mL of ultrapure water for the PM_{2.5} aerosol filters. The insoluble particles were filtrated through the syringe filter (Whatman, PVDF, 0.45 μm). The filtrates were used for the analysis of water-soluble ionic species. A small quantity of filtrates of PM_{2.5} aerosols were fractionated for the analysis of organic acids, and stored in refrigerator at -20°C after adding a few drops of chloroform until the analysis.

The pH of the filtrates was measured with a pH me-

ter (Orion, 720A/81-02 ross electrode, USA), where the pH meter was calibrated using two buffer solutions of pH 4.10 and 6.97.

NH₄⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺ cations were analyzed by IC (Metrohm, Modula IC, Switzerland) with the instrumental conditions of Metrosep Cation-4-150 column, 1.0 mL/min flow rate, 50 μL injection volume, and 4.0 mM HNO₃ eluent. And SO₄²⁻, NO₃⁻, Cl⁻ anions were analyzed using a same IC system with the instrumental conditions of Metrosep A-SUPP-5 column, 0.7 mL/min flow rate, 50 μL injection volume, 1.0 mM NaHCO₃/3.2 mM Na₂CO₃ eluent, and 100 mM H₂SO₄ suppressor solution.

A minute quantity of HCOO⁻, CH₃COO⁻, F⁻ and CH₃SO₃⁻ ions was analyzed using Dionex IC (DX-500, USA) and Metrohm IC. The instrumental conditions for the analysis of those ions were as follows; for Dionex IC, 25 μL injection volume, 2.5 mL/min flow rate, 0.25 mM NaOH/5 mM NaOH eluent (gradient), IonPac AG11/IonPac AS11 column, ASRS suppressor, and for Metrohm IC, 25 μL injection volume, 1.0 mL/min flow rate, 25.0 mM NaOH/3.0 mM Na₂CO₃ eluent, A-SUPP-16 column, 200 mM H₂SO₄ suppressor solution, 55°C column temperature.

The instrumental detection limit (IDL) and coefficient of variation (CV) for the analysis of those water-soluble ions are listed in Table 1.

2.2.2 Elemental Analysis

For the analysis of TSP elemental species, the aerosol samples were decomposed with acids using a microwave digestion system (Milestone, START D, Italy), where aerosol filters were put in a PFA (perfluoroalkoxy) teflon vessel of the microwave oven together with 10 mL acid solution (5.55% HNO₃/16.75% HCl). This vessel was heated at 180°C for 15 minutes with 1000 W microwave radiation to digest the TSP aerosols. The decomposed solution was transferred through syringe filter (Whatman, PVDF, 0.45 μm) into a 25 mL volumetric flask, and the volume was adjusted to 25 mL with 5 mL acid solution (3% HNO₃/8% HCl) and ultrapure water (Mainey and William, 1999).

The number of elements determined by ICP-OES (Perkin Elmer, model OPTIMA 7300DV, USA) and ICP-MS (Perkin Elmer, model ELAN DRC-e, USA)

Table 1. Instrumental detection limit (IDL) and coefficient of variation (CV) for Ion chromatography analysis (n=7).

Species	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻
IDL (μg/L)	3.9-11.9	2.2-9.1	5.3-14.1	4.6-15.1	2.4-14.8	8.1-25.3
CV (%)	1.8-6.1	2.4-3.1	4.2-5.1	4.3-6.5	3.6-4.4	2.2-7.2
Species	NO ₃ ⁻	Cl ⁻	F ⁻	HCOO ⁻	CH ₃ COO ⁻	CH ₃ SO ₃ ⁻
IDL (μg/L)	9.0-11.3	2.2-8.0	1.4-13.9	0.7-1.9	0.9-2.0	1.7-1.8
CV (%)	2.7-3.2	0.9-2.0	0.9-1.2	0.4-1.2	0.6-1.3	1.1-1.2

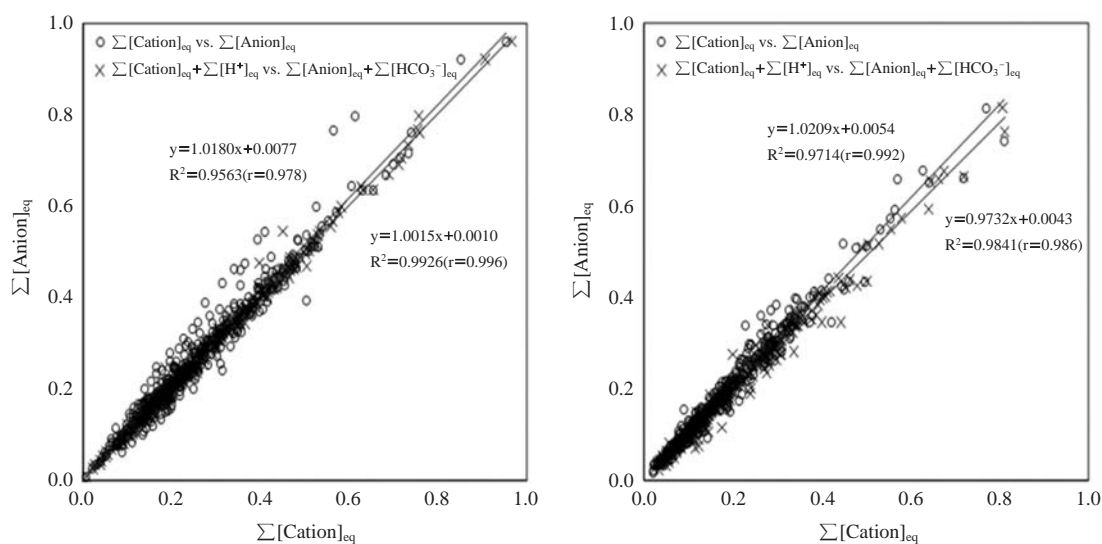


Fig. 1. Cross correlations of $\Sigma[\text{Anion}]_{\text{eq}}$ vs. $\Sigma[\text{Cation}]_{\text{eq}}$ for the analytical data of TSP and $\text{PM}_{2.5}$ aerosols.

instruments was 20 species such as Al, Fe, Ca, Na, K, Mg, Ti, Mn, Ba, Sr, Zn, V, Cr, Pb, Cu, Ni, Co, Mo, Cd, and S. The instrumental conditions of ICP-OES for the analysis of those elements were as follows; 1150 W RF power, 40.68 MHz RF frequency, 0.5 L/min Ar flow, 16.0 L/min coolant, and 1.5 L/min auxiliary. And the instrumental conditions of ICP-MS were as follows; 1500 W RF power, 40 MHz RF frequency, 0.9-1.05 L/min Ar flow, 15.0 L/min coolant, 1.2 L/min auxiliary. For the elemental analysis, the instrumental detection limits (IDL) of ICP-OES were 0.9-47.7 $\mu\text{g/L}$ and those of ICP-MS were in the range of 0.03-0.18 $\mu\text{g/L}$, respectively.

3. RESULTS AND DISCUSSION

3.1 Ion Balance of the Analytical Data

From the ion balance comparison of water-soluble ionic species for the aerosol samples excluding the cases of raining (over 3 mm) and Asian dusts, the correlation coefficients (r) were 0.978 and 0.986, respectively, for the TSP ($n=417$) and $\text{PM}_{2.5}$ ($n=387$) filter samples, indicating a satisfactory correlation. And, for the compensation of H^+ and HCO_3^- concentrations excluded in the ion analysis, pH of the aqueous solutions extracted from TSP and $\text{PM}_{2.5}$ aerosols was measured. The H^+ concentration was reduced from the measured pH values, and HCO_3^- concentration was calculated from the equation (Avila, 1996):

$$[\text{HCO}_3^-] = \frac{K_H \cdot K_1 \cdot p\text{CO}_2}{[\text{H}^+]} = \frac{10^{-11.3}}{10^{-\text{pH}}} = 10^{\text{pH}-11.3}$$

where K_H is the equilibrium constant of CO_2 soluble in H_2O ($3.4 \times 10^{-2} \text{ mol/L} \cdot \text{atm}$), K_1 is the first acid dissociation constant of H_2CO_3 ($4.2 \times 10^{-7} \text{ mol/L}$), and $p\text{CO}_2$ is the partial pressure of CO_2 in air ($3.5 \times 10^{-4} \text{ atm}$). The correlation coefficients for TSP and $\text{PM}_{2.5}$ aerosols from the ion balance comparison including the H^+ and HCO_3^- concentrations were 0.996 and 0.992, respectively, showing better correlations compared to those of the exclusion cases, as in Fig. 1.

3.2 Seasonal Comparison of Aerosol Compositions

3.2.1 Concentrations of Ionic Species

Generally, the meteorological environments like Asian dusts in spring or photochemical reactions in summer may influence the regional atmospheric aerosols, so that the seasonal variations may seriously affect the concentrations of secondary particles such as ammonium, sulfate and nitrate salts in aerosols. Therefore, it has a significant meaning to investigate the seasonal tendencies of the compositions and their concentrations in atmospheric aerosols.

The concentrations of ionic species in TSP and $\text{PM}_{2.5}$ aerosols collected at the Gosan Site during 2008-2011 were classified by seasons as shown in Fig. 2. The concentrations of nss-SO_4^{2-} in TSP for spring, summer, fall and winter were 7.85, 6.55, 6.25, and 6.25 $\mu\text{g}/\text{m}^3$, respectively, showing relatively high values in spring and summer seasons. Similar pattern was found for those in $\text{PM}_{2.5}$ having the values of 6.19, 6.45, 5.57, and 5.40 $\mu\text{g}/\text{m}^3$, respectively. The SO_4^{2-} generation is largely related to the fossil fuel consumption, and its inflow from China continent by the prevailing wester-

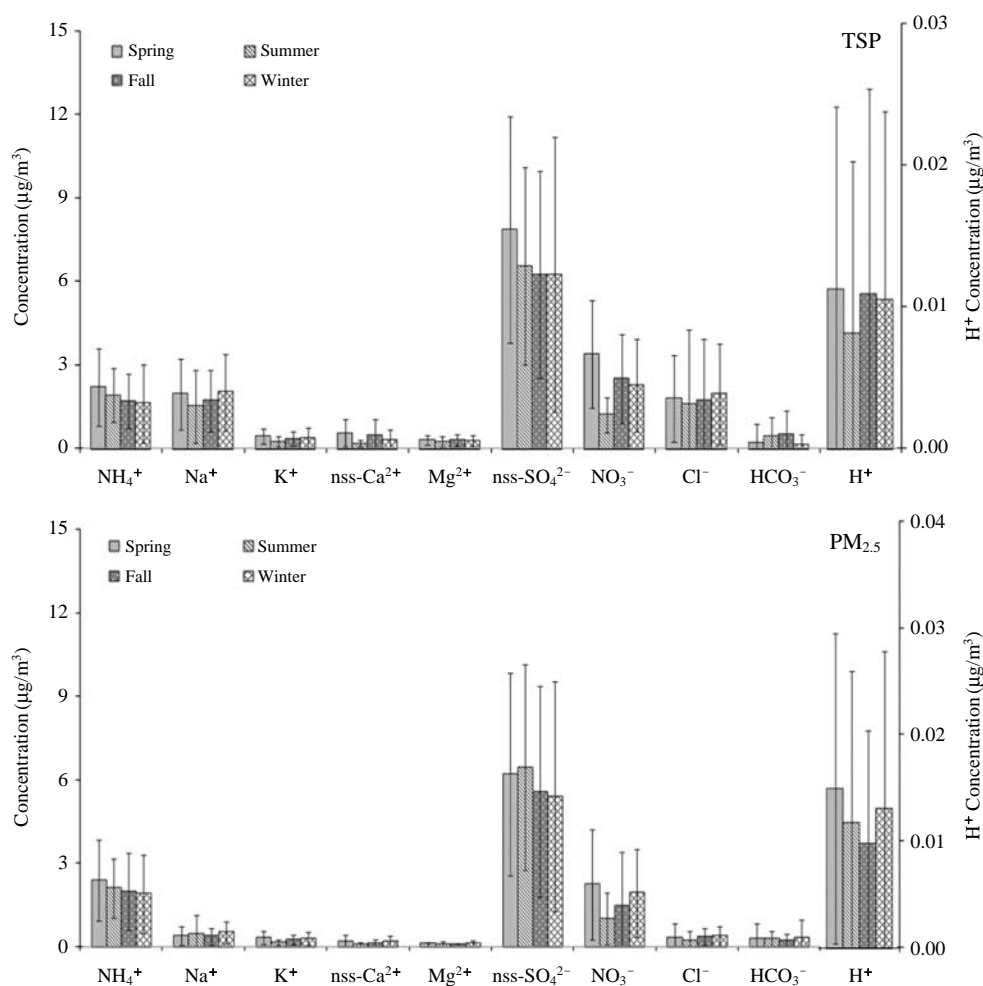


Fig. 2. Ionic concentrations of TSP and PM_{2.5} aerosols in spring, summer, fall and winter.

ly may cause the increase of SO_4^{2-} concentration in spring season. And also, due to the geographical location of the Gosan Site at seashore, the photochemical reaction of DMS (dimethylsulfide) by ultraviolet radiation has been thought to increase the SO_4^{2-} concentration in the early summer of June.

The concentrations of NO_3^- in TSP and PM_{2.5} aerosols for spring, summer, fall and winter were 3.37, 1.20, 2.50, 2.27 $\mu\text{g}/\text{m}^3$, and 2.22, 0.99, 1.47, 1.92 $\mu\text{g}/\text{m}^3$, respectively. The increase of NO_3^- concentration in spring could be reasoned to the external inflows by the prevailing westerly, just like in the case of nss-SO_4^{2-} . And the increase of energy consumption for heating in fall and winter seasons might cause the high NO_3^- concentrations (Kim *et al.*, 2008). The concentrations of NH_4^+ in TSP aerosols for spring and summer were 2.19 and 1.90 $\mu\text{g}/\text{m}^3$, and those in PM_{2.5} aerosols were 2.38 and 2.09 $\mu\text{g}/\text{m}^3$, respectively, which were a bit higher than in other seasons. This could be explained

by the increasing fertilizer usage in spring and the increase of ammonia emission due to the rising temperature in summer.

The concentrations of nss-Ca^{2+} in TSP aerosols for spring and summer were 0.55 and 0.17 $\mu\text{g}/\text{m}^3$, and those in PM_{2.5} aerosols were 0.18 and 0.06 $\mu\text{g}/\text{m}^3$, respectively, showing that its values in TSP and PM_{2.5} for spring are, respectively, 3.2 and 3.0 times higher than for summer. The concentration increase of soil originated nss-Ca^{2+} in spring might be due to the migration of soil components, especially with the Asian dust effect, from China continent by the prevailing westerly (Husar *et al.*, 2001; Park *et al.*, 2001; Kotamarthi and Carmichael, 1993; Iwasaka *et al.*, 1988).

The concentrations of sea-salt originated Na^+ and Cl^- in TSP for winter were 2.01 and 1.95 $\mu\text{g}/\text{m}^3$, and those in PM_{2.5} were 0.50 and 0.35 $\mu\text{g}/\text{m}^3$, respectively, showing the highest among the seasons. It is because the Gosan Site is located just by the western seashore

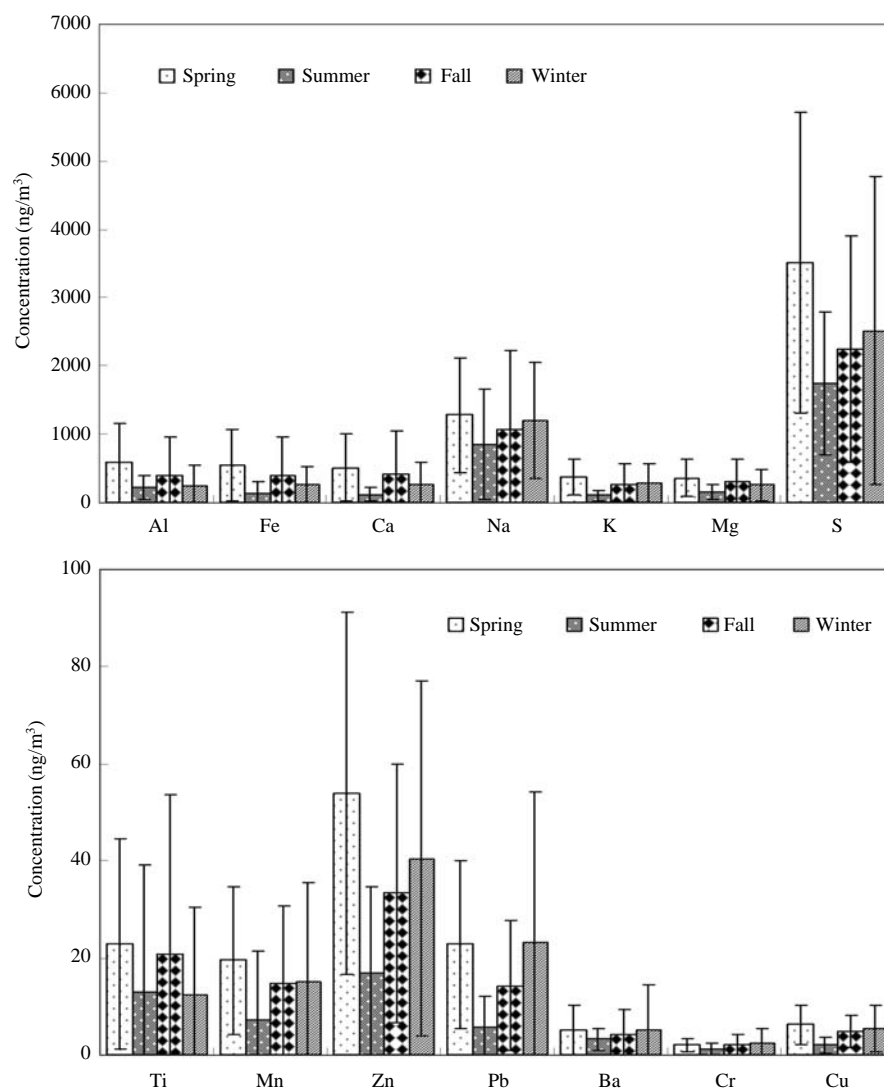


Fig. 3. Elemental concentrations of TSP aerosols in spring, summer, fall and winter.

of Jeju Island, and in winter season, the concentrations of sea-salt components tend to increase due to a high wind speed and active vertical mixing of atmospheric aerosols near seashore area.

The anthropogenic components (nss-SO_4^{2-} , NH_4^+ , NO_3^-) in TSP aerosols have accounted for 72.1, 69.8, 67.4, and 66.7% in spring, summer, fall, and winter, respectively, showing relatively high portion in spring and low in winter. However the sea-salt components (Na^+ , Cl^- , Mg^{2+}) in TSP were 21.6, 24.1, 24.1, and 28.0%, showing the increasing trend in winter contrary to other components. The soil originated nss-Ca^{2+} in TSP aerosols occupied 3.0, 1.2, 3.0, and 1.9% in each season, showing relatively high during spring and fall. On the other hand, the anthropogenic components in $\text{PM}_{2.5}$ aerosols accounted for 87.5, 88.6, 87.4, and 84.2

% in spring, summer, fall, and winter. The sea-salt components in $\text{PM}_{2.5}$ were 6.2, 6.9, 7.4, 8.7%, and the soil nss-Ca^{2+} occupied 1.5, 0.6, 1.1, 1.6%, respectively.

3.2.2 Elemental Concentrations

The elemental components of TSP aerosols at the Gosan Site were analyzed and their concentrations were specified by seasons as shown in Fig. 3. The concentrations of the anthropogenic S in spring, summer, fall, and winter were 3510.4, 1748.0, 2250.8, and 2517.1 ng/m^3 , respectively, showing a high value in spring and low in summer. The concentrations of Na and Mg, which are originated from both sea-salt and soil, were 1276.9, 854.4, 1068.4, 1199.1 ng/m^3 and 358.8, 149.8, 305.3, 259.5 ng/m^3 , respectively, for each season. The concentrations of soil originated Al were 578.7, 224.0,

386.6, 247.2 ng/m³, respectively, showing a high value in spring. And the concentrations of Fe were 541.0, 138.2, 401.0, 266.8 ng/m³, also showing as 3.9 times higher value in spring as in other seasons. The concentration of Ca in spring was 506.1 ng/m³, which was about 4.3 times higher than the summer value (117.6 ng/m³). The concentrations of other soil components, Ti, Ba and Sr, in spring were 22.9, 5.1, and 3.6 ng/m³, respectively, which were much higher than those of other seasons. These all soil originated elements mentioned above showed high concentrations in spring season possibly due to the Asian dust effect.

Furthermore, the elements (S, Pb, Zn) which are reported to be emitted from the anthropogenic sources such as incineration of fossil fuels and combustible trashes, had the composition ratios of 49.3, 52.2, 44.3, and 50.0% in spring, summer, fall, and winter, respectively, showing high values compared to other elements. The composition ratio of the oceanic and soil originated elements (Na, Mg) was high as 29.6% in summer and low as 22.4% in spring. On the other hand, the composition ratios of the soil originated elements (Al, Fe, Ca) were 22.2, 14.2, 23.0, 15.2% in spring, summer, fall, and winter, respectively.

3.3 Acidification and Neutralization Characteristics

3.3.1 Acidification Characteristics

The sulfur oxides (SO_x) and nitrogen oxides (NO_x) undergo through an oxidation reaction to get into atmospheric aerosols as H₂SO₄ and HNO₃, and then, through a reaction with the bases, the sulfate and nitrate salts exist in aerosols as particulate matters. Therefore, it

may be necessary to measure the concentrations of SO₄²⁻ and NO₃⁻ ions, in order to evaluate the approximate extents of acidification by H₂SO₄ and HNO₃. In this study, based on the acidification contributions by major inorganic SO₄²⁻ and NO₃⁻ anions, the correlations between the equivalent concentration sums of [nss-SO₄²⁻]+[NO₃⁻] and [H⁺]+[NH₄⁺]+[nss-Ca²⁺] have been examined for a seasonal basis.

Their correlation coefficients (r) in TSP and PM_{2.5} aerosols were obtained respectively as 0.916-0.939 and 0.924-0.987 in seasons, as shown in Fig. 4, indicating a good correlation. The overall mean slopes between the sums of equivalent concentrations of acidic anions and basic cations in TSP and PM_{2.5} were 1.1288 and 1.0375, respectively, so it was found that the acidic anions had been concentrated a bit more than the basic cations in the atmospheric aerosols. In a seasonal comparison, the slopes for TSP in spring, summer, fall, and winter were 1.0502, 1.1008, 1.1800, 1.1454, and those for PM_{2.5} were 0.9982, 1.0889, 1.0673, 1.0538, respectively. The relatively lower slopes in spring season could be resulted from the increase of nss-Ca²⁺ concentration by the Asian dust.

From the investigation that the organic acids (HCOO⁻, CH₃COO⁻) had contributed as only 5% to the acidification of the atmospheric aerosols, it was confirmed that the acidification might be contributed mainly by the inorganic sulfuric and nitric acids (Hong *et al.*, 2011).

3.3.2 Neutralization Characteristics

The acidic substances in atmosphere are known to be neutralized by the basic substances such as NH₃ and CaCO₃, and their neutralization can be evaluated

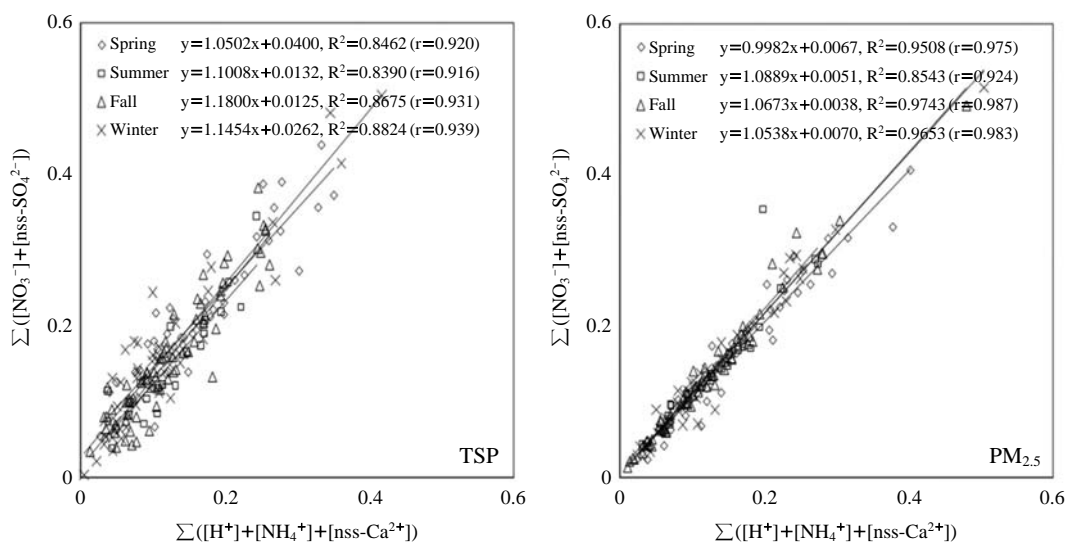


Fig. 4. Correlations between the sums of acidic anions and neutralizing substances in TSP and PM_{2.5} aerosols.

Table 2. Neutralization factors by NH₃ and CaCO₃ in TSP and PM_{2.5} aerosols.

Season	TSP		PM _{2.5}	
	NF _{NH₄⁺}	NF _{Ca²⁺}	NF _{NH₄⁺}	NF _{Ca²⁺}
Spring	0.56	0.12	0.80	0.06
Summer	0.73	0.06	0.78	0.02
Fall	0.58	0.13	0.76	0.05
Winter	0.58	0.07	0.72	0.08
Overall	0.60	0.11	0.77	0.05

by the neutralization factor (NF) from the following equations (Galloway *et al.*, 1989):

$$NF_{NH_4^+} = \frac{[NH_4^+]}{[nss-SO_4^{2-}] + [NO_3^-]}$$

$$NF_{Ca^{2+}} = \frac{[nss-Ca^{2+}]}{[nss-SO_4^{2-}] + [NO_3^-]}$$

Here, [nss-SO₄²⁻], [NO₃⁻], [NH₄⁺], and [nss-Ca²⁺] are the equivalent concentrations of each indicated species. In this study, the neutralization factors have been obtained using the data from the ionic analyses of TSP and PM_{2.5} aerosols and listed in Table 2, and the neutralization ratios by the major basic species have been investigated in a seasonal basis.

The ammonia contributes to the neutralization in atmosphere to a great extent. The neutralization ratios by NH₃ in TSP and PM_{2.5} aerosols were found as 59.8 % and 76.5%, respectively, showing much more neutralization contribution in PM_{2.5}. On the other hand, the neutralization ratios by CaCO₃ were 10.5% and 5.5% respectively in TSP and PM_{2.5} aerosols, showing a contrary result to that by NH₃.

Seasonally, in TSP aerosols, the neutralization ratios by NH₃ in spring, summer, fall, and winter were 56.3, 73.3, 58.3, 58.5%, and those by CaCO₃ were 12.4, 6.2, 12.8, 7.4%, respectively, showing high neutralizations by NH₃ in summer and by CaCO₃ in spring and fall. On the other hand, in PM_{2.5} aerosols, the neutralization ratios by NH₃ in spring, summer, fall, and winter were 79.6, 78.3, 76.4, 72.5%, and those by CaCO₃ were 6.4, 2.3, 4.5, 7.5%, respectively, indicating almost no discrepancy by NH₃ through the seasons but relatively a bit high neutralizations by CaCO₃ in spring and winter.

3.4 Pollution Characteristics

3.4.1 Emission Sources of the Atmospheric Aerosols

The rotated Varimax factor analysis has been carried out using a statistical program (SPSS 12) in order to identify emission sources and characteristics of the atmospheric aerosols (Oravisjarvi *et al.*, 2003; Kang

Table 3. Results of rotated Varimax factor analysis for TSP components.

Species	Factor 1	Factor 2	Factor 3
NH ₄ ⁺	-0.01	0.81	-0.15
Na ⁺	0.06	0.04	0.95
K ⁺	0.11	0.85	0.07
nss-Ca ²⁺	0.78	0.38	0.24
Mg ²⁺	0.34	0.09	0.88
nss-SO ₄ ²⁻	0.07	0.83	-0.11
NO ₃ ⁻	0.38	0.54	0.38
Cl ⁻	0.08	-0.15	0.90
Al	0.93	0.17	0.11
Fe	0.93	0.25	0.15
Ca	0.88	0.29	0.23
Na	0.31	0.07	0.86
K	0.64	0.67	0.16
Mg	0.82	0.16	0.50
S	0.32	0.80	0.06
Ti	0.75	-0.07	0.18
Mn	0.76	0.42	0.07
Zn	0.28	0.84	0.05
Pb	0.21	0.82	0.07
Ba	0.43	0.49	0.05
Cr	0.27	0.21	0.03
Cu	0.38	0.62	0.10
Eigenvalue	6.4	6.1	3.9
Variance (%)	28.9	27.6	17.7
Cumulative (%)	28.9	56.5	74.1

Table 4. Results of rotated Varimax factor analysis for PM_{2.5} components.

Species	Factor 1	Factor 2	Factor 3
NH ₄ ⁺	0.96	-0.04	0.14
Na ⁺	-0.01	0.93	0.11
K ⁺	0.79	-0.01	0.32
nss-Ca ²⁺	0.36	-0.02	0.89
Mg ²⁺	0.19	0.44	0.79
nss-SO ₄ ²⁻	0.91	-0.07	0.12
NO ₃ ⁻	0.62	0.23	0.30
Cl ⁻	0.00	0.92	0.11
Eigenvalue	2.9	2.0	1.7
Variance (%)	36.8	24.6	20.9
Cumulative (%)	36.8	61.4	82.3

et al., 2003; Roscoe *et al.*, 1982).

For the components in TSP aerosols, showing the overall cumulative factor loadings as 74.1% explanation as in Table 3, the first factor with 28.9% explanation might be considered as a soil originated source due to high loadings of nss-Ca²⁺, Al, Fe, Ca, Mg, Ti, Mn species. The second factor with 27.6% explanation have loaded largely by NH₄⁺, K⁺, nss-SO₄²⁻, S, Zn, Pb species, which are mostly emitted from anthropogenic sources such as automobiles, heating fuels and industries. The third factor with largely Na⁺, Mg²⁺,

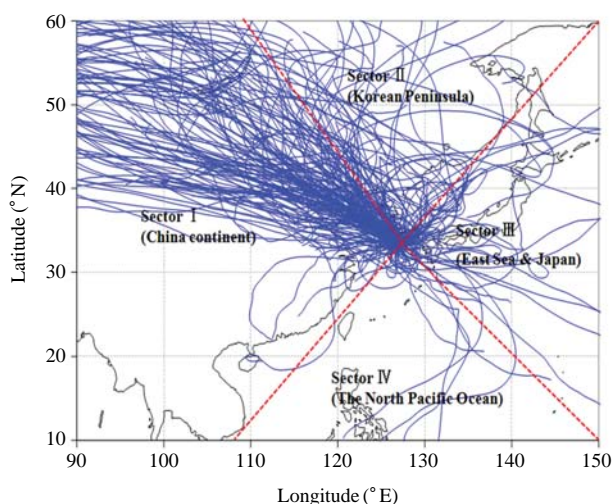


Fig. 5. 5-Day backward trajectories at the Gosan Site of Jeju Island during the study period.

Cl^- , and Na loadings would be due to sea-salt effect.

For $\text{PM}_{2.5}$ aerosols shown in Table 4, the first factor with 36.8% out of overall 82.3% explanation have highly loaded NH_4^+ , K^+ , and nss-SO_4^{2-} which are mostly produced from anthropogenic origins. The second factor with 24.6% explanation has loaded the oceanic Na^+ and Cl^- , and the third factor with 20.9% explanation has loaded the soil originated nss-Ca^{2+} and Mg^{2+} species.

From the above results of the factor analysis, the atmospheric aerosols at Gosan area of Jeju Island could be thought to be influenced largely by the soil sources in TSP and the anthropogenic sources in $\text{PM}_{2.5}$.

3.4.2 Inflow Pathways of Air Mass

The five-day backward trajectories have been performed to investigate the inflow pathway of the air mass into the Gosan Site, and it was ascertained using the HYSPLIT4 (HYbrid Single Particle Lagrangian Integrated Trajectory) model of National Oceanic and Atmospheric Administration (NOAA) (Draxler and Rolph, 2013; Kim *et al.*, 2008). The air mass inflow pathways have been classified by four sectors as shown in Fig. 5; China continent (Sector I), Korean peninsula (Sector II), East Sea & Japan (Sector III), and North Pacific Ocean (Sector IV). The sectional frequencies of air mass inflow into the Gosan area were 80.0% (Sector I), 11.9% (Sector II), 3.8% (Sector III), and 4.3% (Sector IV) during the study, showing a significant influence from China continent.

The sectional concentrations of major ionic species in TSP and $\text{PM}_{2.5}$ aerosols were listed in Table 5 and 6. For TSP aerosols, nss-SO_4^{2-} concentrations were in the order of Sector I ($7.07 \mu\text{g}/\text{m}^3$) > Sector II ($6.58 \mu\text{g}/\text{m}^3$) > Sector III ($5.59 \mu\text{g}/\text{m}^3$) > Sector IV ($2.81 \mu\text{g}/\text{m}^3$),

Table 5. Sectional concentrations of ionic components in TSP.

Species	Concentration ($\mu\text{g}/\text{m}^3$)			
	Sector I	Sector II	Sector III	Sector IV
NH_4^+	1.92	1.77	1.67	0.66
Na^+	1.83	1.39	2.20	2.06
K^+	0.38	0.33	0.23	0.15
nss-Ca^{2+}	0.45	0.31	0.13	0.12
Mg^{2+}	0.28	0.22	0.36	0.25
Cl^-	1.80	0.91	2.88	1.91
NO_3^-	2.67	2.05	1.21	2.14
nss-SO_4^{2-}	7.07	6.58	5.59	2.81

Table 6. Sectional concentrations of ionic components in $\text{PM}_{2.5}$.

Species	Concentration ($\mu\text{g}/\text{m}^3$)			
	Sector I	Sector II	Sector III	Sector IV
NH_4^+	2.15	2.14	1.64	1.29
Na^+	0.40	0.26	0.54	0.72
K^+	0.27	0.20	0.11	0.09
nss-Ca^{2+}	0.15	0.12	0.04	0.08
Mg^{2+}	0.08	0.07	0.07	0.10
Cl^-	0.33	0.22	0.40	0.16
NO_3^-	1.77	1.76	0.87	1.66
nss-SO_4^{2-}	5.99	5.77	4.90	4.26

showing the highest with the air mass inflow from China continent. Similarly, the concentrations of NH_4^+ , NO_3^- and nss-Ca^{2+} were also high when the air masses had been moved from Sector I. The concentrations for $\text{PM}_{2.5}$ aerosols showed almost the same trend as the case of TSP. This explains that most of the air masses are moved from China continent and seriously affect the air quality of Jeju Island.

4. CONCLUSIONS

The ion balances of the water-soluble ions in TSP and $\text{PM}_{2.5}$ atmospheric aerosols collected at the Gosan Site of Jeju Island have shown good correlations as 0.996 and 0.992, respectively. For TSP aerosols, the concentrations of nss-SO_4^{2-} were high in spring and summer, and those of NO_3^- , NH_4^+ , and most of elemental species showed high concentrations in spring. On the other hand, most components in $\text{PM}_{2.5}$ aerosols showed high concentrations in spring season, except high nss-SO_4^{2-} in summer. In TSP, the neutralization by NH_3 increased in summer and that by CaCO_3 increased in spring and fall, however there is almost no discrepancy by seasons in $\text{PM}_{2.5}$. The factor analysis

has resulted that the TSP aerosols are originated preferentially by soil, followed by anthropogenic and marine sources, but the PM_{2.5} aerosols have a different pattern as mainly anthropogenic and followed by marine and soil sources. The backward trajectory analysis has confirmed that the major aerosol species such as nss-SO₄²⁻, NO₃⁻, NH₄⁺, S, Pb, Zn, etc. are delivered as the air masses have moved from the China continent.

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