

Characterization of chemical properties of atmospheric aerosols over Anmyeon (South Korea), a super site under Global Atmosphere Watch

Sung-Hwa Park · A. S. Panicker · Dong-In Lee ·
Woon-Seon Jung · Sang-Min Jang · Min Jang ·
Dongchul Kim · Yu-Won Kim · Harrison Jeong

Received: 23 March 2011 / Accepted: 17 October 2011 /

Published online: 17 December 2011

© Springer Science+Business Media B.V. 2011

Abstract This paper reports aerosol chemical properties for the first time over a Korean Global Atmosphere Watch (GAW) supersite, Anmyeon (36°32'N; 126° 19'E), during 2003–2004 period. Total suspended Particulates (TSP) showed significant seasonal variation with consistent higher mass concentrations during spring season (average of up to $230 \pm 190 \mu\text{g}/\text{m}^3$). PM_{10} also followed similar trend with higher concentrations during spring (average of up to $170 \pm 130 \mu\text{g}/\text{m}^3$) and showed reduced concentrations during summer. $\text{PM}_{2.5}$ showed a significant increase during summer (average of up to $60 \pm 25 \mu\text{g}/\text{m}^3$), which could be due to the influx of fine mode sea salt aerosols associated with the Changma front (summer monsoon). Chemical composition analysis showed enhanced presence of acidic fractions, majorly contributed by sulphates (SO_4^{2-}) and nitrates (NO_3^-) in TSP, PM_{10} and $\text{PM}_{2.5}$ during different seasons. Enhanced presence of Calcium (Ca^{2+}) was observed during sand storm days during spring. The high correlation obtained on matrix analysis between crustal ions and acidic ions suggests that the ionic compositions over the site are mainly contributed by

S.-H. Park · S.-M. Jang · M. Jang

Atmospheric Environmental Research Institute, Pukyong National University, Busan, South Korea

A. S. Panicker · D.-I. Lee (✉)

Department of Environmental Atmospheric Sciences, Pukyong National University,

599/1 Daeyong 3 Dong, Nam GU, Busan, South Korea 608737

e-mail: leedi@pknu.ac.kr

W.-S. Jung

Interdisciplinary Program of Earth Environmental Engineering, Pukyong National University, Busan, South Korea

D. Kim

Goddard Earth Sciences and Technology Center, University of Maryland Baltimore County, Baltimore, MD, USA

D. Kim

Universities of Space Research Association, Columbia, Maryland, USA

Y.-W. Kim · H. Jeong

Korea Global Atmosphere Watch Center, Korea Meteorological Administration, Seoul, South Korea

terrestrial sources of similar origin. The neutralization factors has been estimated to find the extend of neutralization of acidity by main basic components, and found to have higher value for Ammonium (up to 1.1) in different seasons, indicating significant neutralization of acidic components over the region by NH_4^+ . Back trajectory analysis has been performed during different seasons to constrain the possible sources of aerosol origin and the results are discussed in detail.

Keywords Aerosols · TSP · PM_{10} · $\text{PM}_{2.5}$

1 Introduction

Aerosols are important atmospheric constituents due to of their impact on air quality and also because of their role in inducing climate change. Aerosols influence heat balance of the Earth, directly by reflecting and absorbing solar radiation and indirectly through altering the cloud microphysics (Twomey 1977; Panicker et al. 2010a, b). They influence human health by inducing adverse respiratory effects. Particulate Matter (PM) is the term used for particles found in the air including dust, dirt, soot, smoke and liquid droplets coming in a wide range of sizes. The main particulate pollutants in terms of size fraction has been mainly classified as PM_{10} (Particulate matter including all particles below a diameter of 10 μm), $\text{PM}_{2.5}$ (Particulate matter including all particles below a diameter of 2.5 μm). PM_{10} particles are small enough to get into the lungs and can trigger or aggravate respiratory conditions such as asthma and bronchitis. $\text{PM}_{2.5}$, which are referred as “fine particles,” have highest probability of deposition deeper in the respiratory tract and can cause even death (Fang et al. 1999). Increasing pollutant emissions associated with the fast-growing economies of Southeast Asian countries have led to the progressive increase of aerosol concentrations above the natural background (Gautam et al. 2009). South Korea is an economically developed and highly industrialized country in south-east Asia. Since the increased industrialization has been inducing continuous pollution, it is necessary to constantly monitor such pollution effects. In this perspective, a Global Atmosphere Watch (GAW) observatory is established at a super site in Anmyeon Island in the western part of South Korea. The GAW center is characterized with meteorological and pollutant observations. In this study we present the observed size segregated aerosol particle (TSP, PM_{10} and $\text{PM}_{2.5}$) variation and their chemical composition for the first time over Anmyeon in different seasons during 2003–2004 periods.

2 Experimental site and instrumentation

2.1 Meteorology of the location

The Anmyeon (36° 32'N; 126° 19'E, H: 45.7 m ASL) is a back ground island station located in the western cape of South Korea. It has been an important Global Atmosphere Watch (GAW) center associated with the region II of World Meteorological Organization (W.M.O) over Asia. The prevailing meteorological conditions of the site during different months are depicted in Table 1. The Annual mean temperature found to be 12–12.6°C over the site. The winter season is characterized with lower temperature (–3.5 to 2°C) and with comparatively lower humidity ranges (60–70%). The site experiences yellow sand and dust associated with dust storm events during spring. The precipitation is higher in summer

Table 1 Meteorological conditions at Amyeon-Do during 2003 and 2004

Year	Pressure (hPa)		Temperature (°C)		Humidity (%)		Precipitation (mm)		Wind speed (m/s)		Wind direction	
	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004	2003	2004
Jan.	1021.2	1021.4	-3.5	-1.8	74	69	20.9	27.3	2.5	2.1	NNW	ENE
Feb.	1019.7	1017.5	0.9	1.7	75	66	39.0	26.3	2.3	3.3	ENE	SSW
Mar.	1018.5	1017.6	4.6	4.9	70	60	22.5	15.7	2.5	3.3	NE	SSW
Apr.	1012.3	1011.3	11.7	11.1	70	62	180.0	80.2	2.9	3.1	SSW	SSW
May	1009.6	1006.9	18.2	16.6	70	73	105.5	140.3	2.3	3.1	ENE	SSW
Jun.	1003.5	1006.9	20.8	21.9	78	72	221.8	211.1	2.4	2.2	SSW	SSW
Jul.	1003.9	1004.2	23.5	24.8	84	84	290.2	321.9	2.3	3.2	SSW	SSW
Aug.	1006.0	1004.9	23.7	26	85	78	257.9	131.2	2.4	2.1	SSW	ENE
Sep.	1010.9	1011.6	20.5	21.3	82	76	201.9	282.6	2.2	2.1	ENE	ENE
Oct.	1015.7	1018	13.2	14.2	71	65	23.0	1.8	2.3	2.2	ENE	ENE
Nov.	1019.8	1020.1	8.9	8.1	73	75	53.6	70.5	2.4	1.9	ENE	NE
Dec.	1021.9	1022.2	1	2.1	70	66	17.1	32.0	2.7	2.4	NNW	NE
Ann.	1013.6	1013.6	12	12.6	75	71	1433.4	1340.9	2.4	2.6	ENE	SSW

season with peak rainfall during July, associated with the summer monsoon (Changma). The site obtains both marine as well as continental air masses during different seasons. The wind directions used to be from south-west direction during summer season, carrying abundant sea salt nuclei to the land areas. Anmyeon-do has been maintained as a background site according to W.M.O criterion for GAW observatories (W.M.O/GAW 2004) to carry out observations of aerosols, air pollution, radiation and meteorological parameters.

2.2 Instrumentation and sampling

A high volume air sampler (Anderson Inc, GMB2360, U.S.A) was operated in different seasons during 2003–2004 period for collecting TSP and PM₁₀ concentrations. TSP and PM₁₀ samples were collected on Whatman No. 41 filter papers of size 8 in by 10 in. The average flow rate of sampling was about 1.2 m³/min and the sampling duration for each sample was about 24 h. PM_{2.5} was collected using a BRABO (TCR Tecora) sampler operated at an average flow rate of 20 l/min using Whatman 1851–047 filter paper. Data quality control over the site for aerosol sampling and analysis has been maintained according to W.M.O standards for Global Atmosphere watch sites (W.M.O/GAW 2004).

The sampled filter papers were equilibrated for humidity before and after the weighing. Corresponding filter papers of TSP, PM₁₀ and PM_{2.5} were extracted for water soluble chemical components and further analyzed for ionic species extractions. For performing water soluble analysis, Soxhlet extractors were used, consisting of three parts, namely, a distillation flask, an extractor and a reflux condenser. All the parts are connected by ground glass joints. The known quantity of extracting solvent (distilled water in case of water soluble components) was poured into the distillation flask in which pieces of the filter paper to be extracted were kept. It was made to boil in the heating mantle. The vapors of the solvent were led to the extractor through a wider tube and then reflux condenser. A flow of cool water was kept running around the condenser through the inlet and outlet. The vapors got condensed and the solvent drained down into the extractor thimble. Gradually, the

extractor became filled with the solvent. When the level of the liquid reached the upper part of the siphon, it automatically drained into the flask. The same process was continuously repeated for 45 min to get the maximum extraction. Then the solutions were cooled and filtered through a Whatman 41 filter paper. They were then stored in a polyethylene bottle and kept in refrigerator until the completion of the chemical analysis. 31 samples of TSP were analyzed during 2003 and 58 samples were analyzed during 2004. 21 and 58, PM_{10} samples were used respectively in 2003 and 2004. 16 and 21 $PM_{2.5}$ samples were analyzed during 2003 and 2004.

Chemical analysis of both anions and cations (Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) were carried out using an Ion Chromatograph (Dionex Inc. ICS-2000). The ICS-2000 system is a totally integrated and preconfigured Reagent-Free Ion Chromatography system with Eluent Generation (RFIC-EG system) designed to perform all types of electrolytically generated isocratic and gradient IC separations using conductivity detection. Potassium hydroxide (KOH) was used as eluent for anion analysis and cation analysis were performed using methane sulfonic acid (MSA) as eluent. The detection limit for ion chromatographic analysis was about 0.01 ppm. The ratio of average equivalent sum of anions to that of cations ($\sum anions/\sum cations$) found to be 1.036 ± 0.269 , suggesting all the important ionic constituents have been measured (Al-Khashman 2005; Wang and Han 2011).

3 Results and discussions

3.1 Seasonal variation of TSP and particulate matter

Figure 1 depicts air mass back trajectory (5 day) on different experimental days during 2003–2004. During spring air mass trajectories were directed from north-north west directions, carrying mainly absorbing dust aerosols from arid regions of Mongolia and China. The site experiences heavy sand/yellow dust storms associated with the inflow of absorbing yellow dust from these arid regions during spring. Along with these, air mass also directed from East Sea, during the season, which can carry sea salt aerosols of marine origin to the location. During summer the air mass trajectory is mainly directed from south-south west directions, associated with the inflow of Changma front (summer monsoon). This south west wind brings sea salt aerosols from adjacent oceanic areas. During autumn and winter, prominent back trajectories were observed from north west directions indicating long range transport of particulates from China and Mongolia, consisting mainly absorbing desert dusts. The possible anthropogenic aerosol sources reaching the site could be transported aerosols due to mechanical production, automobile exhaust and from adjacent factory exhausts. However since the site has been maintained as a clean background site, the possibility of anthropogenic aerosols generated within the island is sparse.

The mass concentration of total suspended particulates (TSP) during 2003 and 2004 in different seasons over Anmyeon-do are shown in Fig. 2. TSP concentrations found to be high during 2004, could essentially be associated with more sand storm days during 2004 compared to 2003. TSP showed higher values during spring. TSP values generally found to be in the range of 130–190 $\mu g/m^3$ during different experimental days in spring. However, anomalous values of TSP (up to 530 $\mu g/m^3$) were observed on dust storm days (highlighted in Fig. 1), indicating enhanced transport of dust/yellow sand, similar as Kosa dust (Watanabe et al. 2006; Mori et al. 1998), from adjacent deserts, leaving mean value of TSP very high ($230 \pm 190 \mu g/m^3$) in spring, as suggested by Kim et al. (2001). TSP

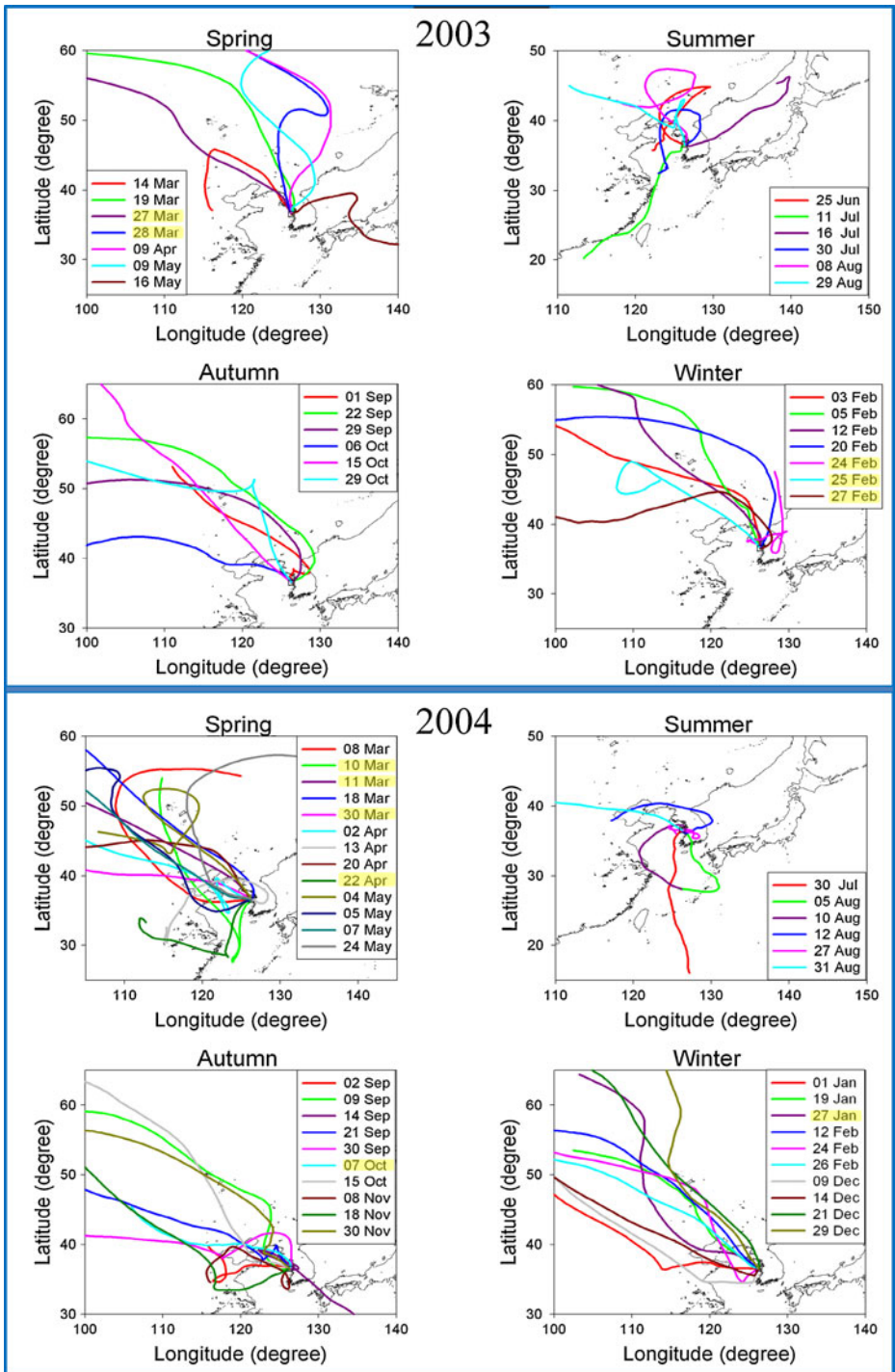


Fig. 1 Back trajectory showing air mass on different observational days during different seasons (dust storm days are highlighted)

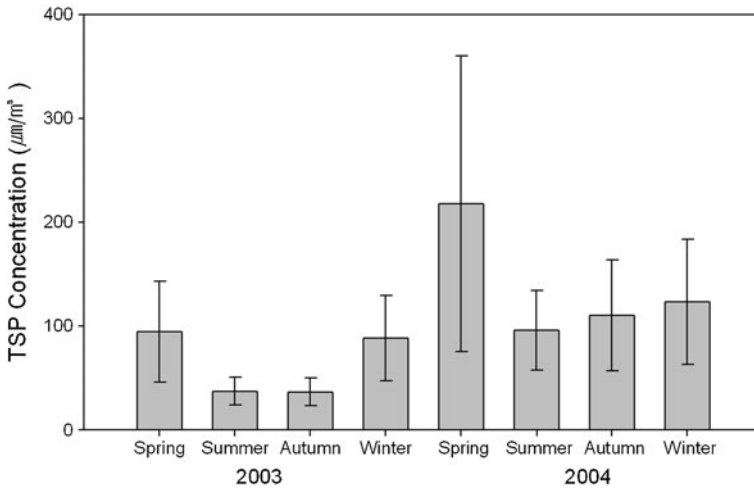


Fig. 2 Seasonal variations of TSP concentrations over Anmyeon-do during 2003 and 2004

concentration observed here found to be higher than that reported over certain other back ground sites in Asia (Safai et al. 2002, 2005; Chatterjee et al. 2010). TSP found to be lowest during summer, which could be associated with the rain out and washout of atmospheric particles associated with the precipitation events during Changma (monsoon) season (Fig. 2). There was an enhancement in TSP concentration during autumn, which found to be gradually increasing to spring through winter. PM_{10} concentrations also followed the same trend with lowest value during summer, followed by an enhancement in autumn and winter with highest mass concentration in spring (Fig. 3). Anomalous high values of TSP and PM_{10} were also observed on winter during dust storm days (Fig. 1), which could be associated with the enhanced transport of yellow sand during these days (Kim and Park 2001). Highest PM_{10} concentrations were observed in spring ($170 \pm 130 \mu\text{g}/\text{m}^3$), and found to have lowest mean values during summer ($34 \pm 15 \mu\text{g}/\text{m}^3$). $PM_{2.5}$ concentrations also showed enhancement up to $60 \pm 25 \mu\text{g}/\text{m}^3$ during spring (Fig. 4).

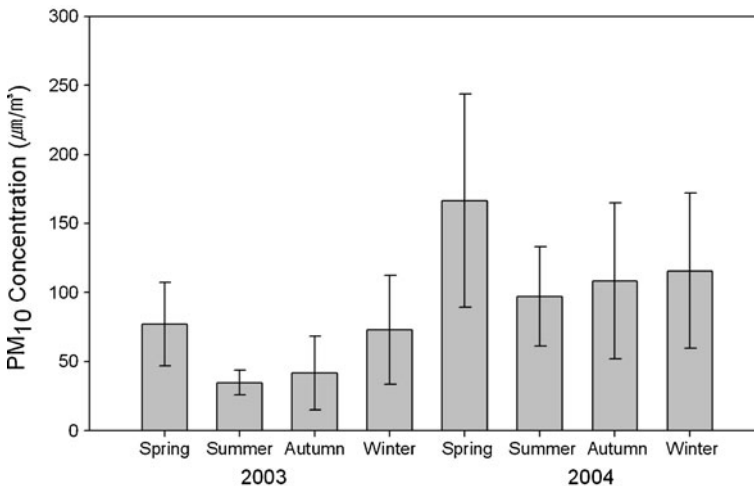


Fig. 3 Seasonal variation of PM_{10} concentrations over Anmyeon-do during 2003 and 2004

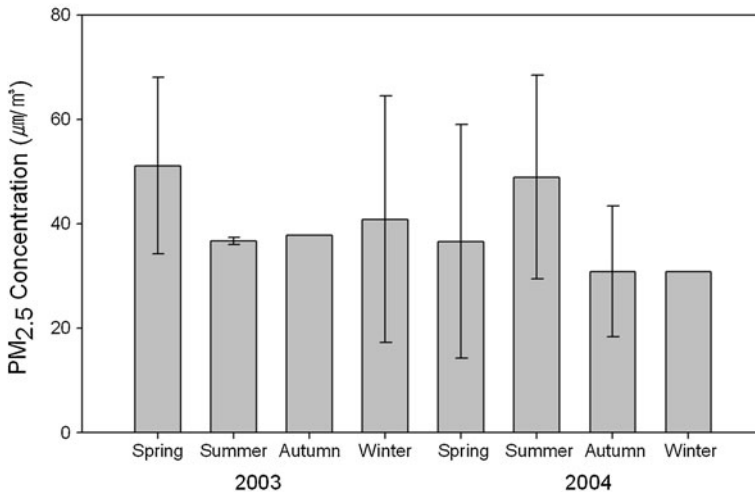


Fig. 4 Seasonal variation of PM_{2.5} concentrations over Anmyeon-do during 2003 and 2004

Higher PM_{2.5} concentrations were observed in 2004 during summer. This could be associated with the large influx of fine and near coarse mode sea salt particles from adjacent oceans, associated with Changma front during summer, as indicated by back trajectory analysis (Fig. 1).

3.2 Variation of chemical composition of TSP and particulate matter

The chemical composition of TSP and particulate matter were analyzed using ion chromatograph as explained in Section 2. Acidic components such as sulfates (SO₄²⁻) and nitrates (NO₃⁻) showed major concentration in TSP as well as in particulate matter (PM₁₀ and PM_{2.5}) in all seasons. In TSP, sulfate concentration varied from 6.24±4 µg/m³ to 22.5±11 µg/m³ in different seasons (Fig. 5), contributing to 25–41% of the TSP mass. The nitrate fraction found to be contributing to 22–44% (6.12 µg/m³ to 16.45 µg/m³) in different seasons. Fluorides (F⁻) and chlorides (Cl⁻) mass in TSP found to be nominal (4–9%) in different seasons. The concentration of basic components were found to be less in TSP. Ammonium (NH₄⁺) was the major basic component observed in TSP, which contributes to 7–22% (1.6 µg/m³ to 11.9 µg/m³) of the total TSP mass. The ammonium content found to be higher during summer season (up to 22%). Sodium (Na⁺) found to be the second cationic species having major contribution to TSP in different seasons (4–7%). The mass concentration of potassium (K⁺), magnesium (Mg²⁺) and calcium (Ca²⁺) found to be nominal (1–5%). However enhanced concentration of calcium was observed on the sand storm days (highlighted in Fig. 1), suggesting Ca²⁺ is a major component in desert dust. Wang et al. (2006) also reported enhanced Ca²⁺ during dust storm days over Beijing in China. Overall, sulfates, nitrates and other anions found to be contributing up to 50–70% of the TSP concentration among the water soluble components in all seasons, and hence leaving the atmospheric composition “Acidic” in nature. PM₁₀ also showed the same features with a majority of sulfates and nitrates indicating strong acidic deposition in the atmosphere (Fig. 6).

Since Anmyeon-do is maintained as a clean background site, primary emissions cannot be a potential contributor for higher sulfate concentration in TSP and particulate matter. A possible mechanism for high acidic sulfate concentration could be aqueous-phase oxidation

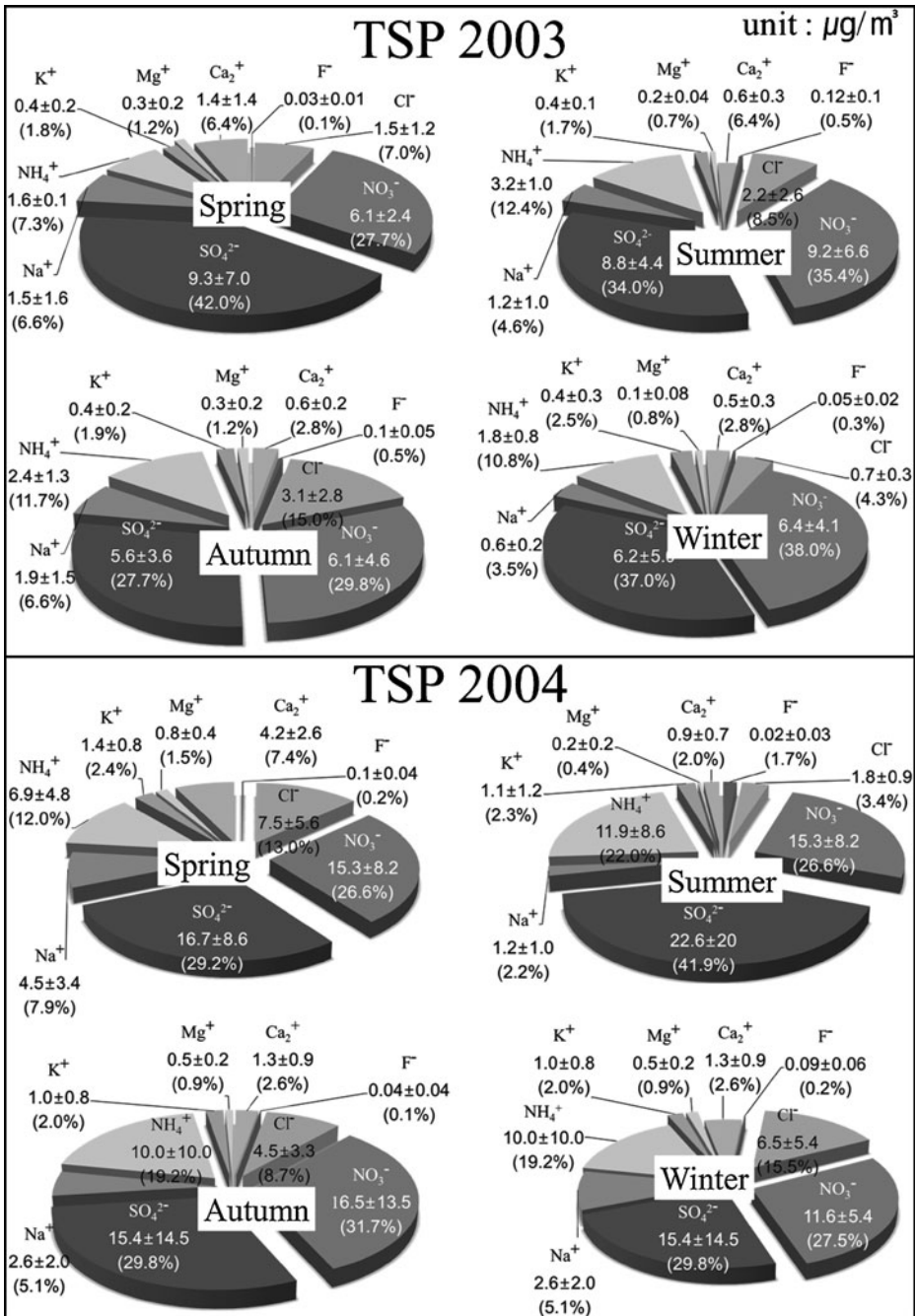


Fig. 5 Variation of Mass concentrations of different ionic species in TSP, during different seasons

of SO_2 in cloud droplets (Seigneur and Saxena 1988), along with the prominent gas to particle conversion processes. The reason for the origin of fine mode sulphate

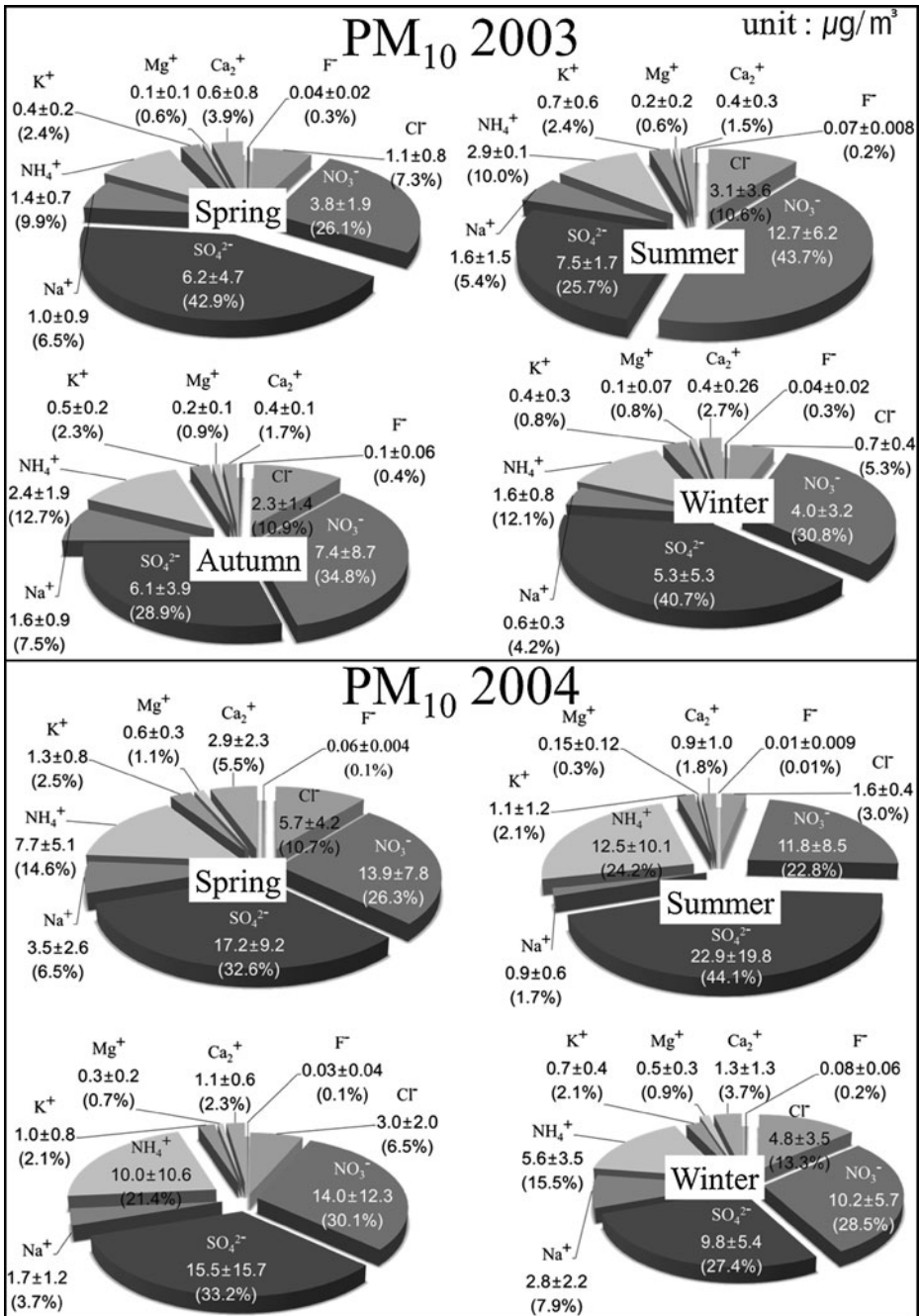


Fig. 6 Variation of Mass concentrations of different ionic species in PM₁₀, during different seasons

concentrations could be associated with the oxidation of SO₂ released from adjacent factories, or may be from conversion of biologically emitted sulfur gases like dimethyl sulfide (Uematsu et al. 2010) transported to the experimental area. The major mechanism of

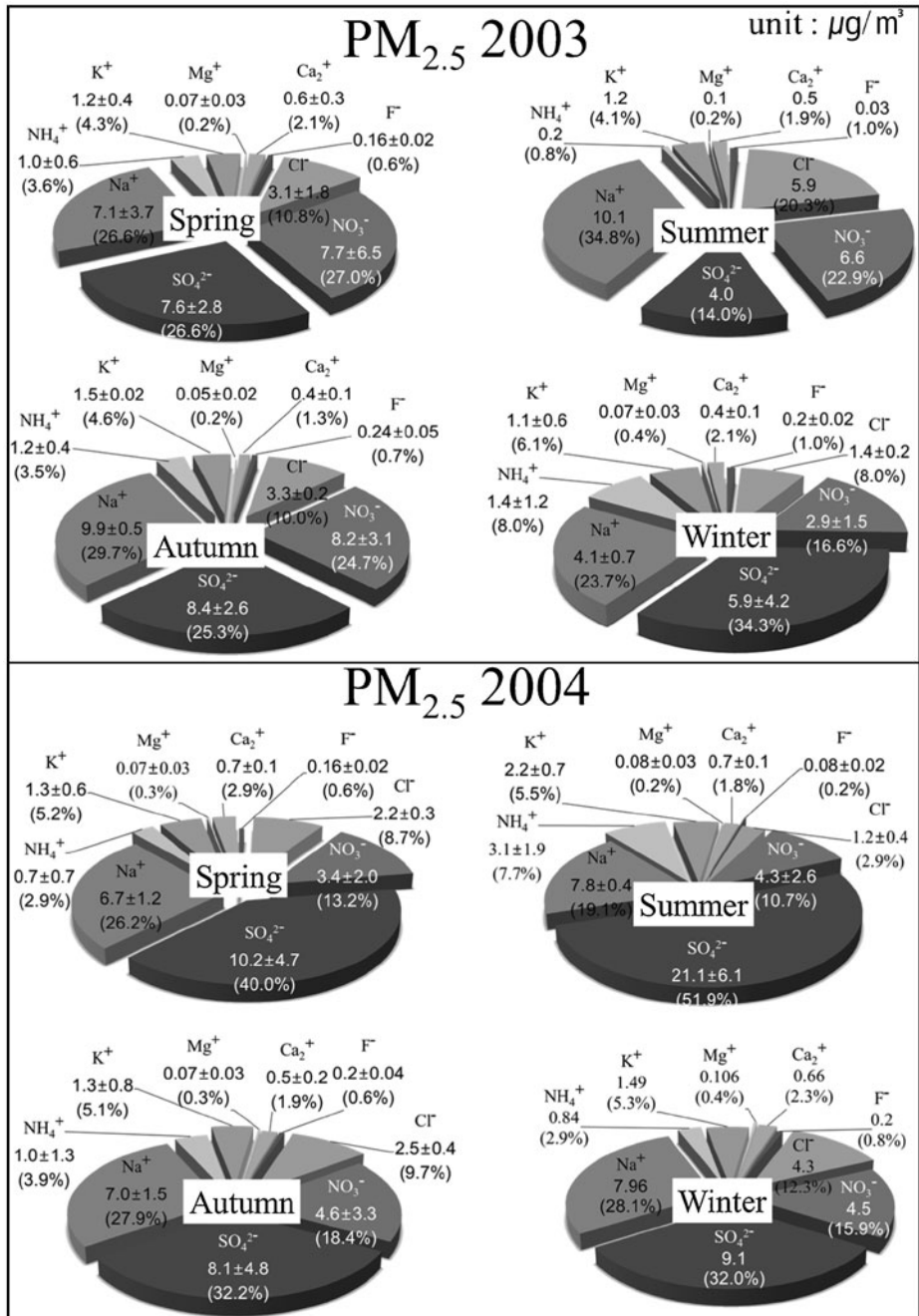


Fig. 7 Variation of Mass concentrations of different ionic species in PM_{2.5}, during different seasons

nitrate formation could be associated with the homogeneous gas-phase transformation of NO_x to HNO₃, followed by the reaction with NH₃ to form NH₄NO₃ as explained by Seinfeld and Pandis (1998). Fluoride (F⁻) may be contributed by transported emissions from industrial

activities around the experimental site. Particulate ammonium (NH_4^+) may originate by the reaction of NH_3 vapors with acidic gases such as H_2SO_4 , HNO_3 and HCl . Increase in human population and activities related to animal husbandry may be other main reasons for the increase in NH_4^+ . Normally, soil is considered to be the main source of potassium (Mouli et al. 2006). Vegetative emissions could be another important source for K^+ aerosols.

$\text{PM}_{2.5}$ also showed a majority of acidic composition (Fig. 7), with sulphate concentrations up to 50% during summer. However an enhanced contribution from NH_4^+ and sodium (Na^+) is found to be neutralizing acidity in all seasons. Along with sulfates and nitrates, chlorides also found to be a major contributor in $\text{PM}_{2.5}$ concentration. Potassium contribution also found to be higher in $\text{PM}_{2.5}$, compared to TSP and PM_{10} . The fine particles of K^+ may be released into the atmosphere by burning of plant material (Cooper 1980); however, vegetation might have act as another source of K^+ particles through guttation (Kleinman et al. 1979). The contribution of basic components, such as Mg^{2+} and Ca^{2+} found to be less (2–5%) compared to that reported over other back ground regions and pristine oceanic environments (Safai et al. 2005; Rao et al. 2001). Generally soil is considered to be the main source of both Mg^{2+} and Ca^{2+} . However observed anomalous high Ca^{2+} values during sand storm days suggests that yellow sand also is a source of Ca^{2+} . Zang et al. (2003) reported that 6% of Asian dust is contributed by Ca^{2+} . In spite of being maintained as a background clean site, the enhanced acidic deposition over Anmyeon-do may be associated with the transported acidic components from adjacent factories surrounding the island. Uematsu et al. (2010) performed aerosol chemical composition analysis over East China Sea and found that nss SO_4^{2-} and NO_3^- are prominent acidic component along with heavy metals such as Al, Zn, Mn, and Pb. A long term trend analysis of aerosol chemical composition over Jeju, Korea (Ko et al. 2011) revealed that nss SO_4^{2-} is the dominant component. It also has been found that NO_3^- , have considerably increased in the last decade compared to SO_4^{2-} . Na^+ and NH_4^+ found to be the most prominent neutralizers over Jeju. Zhou et al. (2009) reported enhanced sulphate content in another East Asian site with its pre dominance during summer. The occurrence of high value of some components (e.g.: Na^+ , Ca^{2+}) in $\text{PM}_{2.5}$ compared to TSP and PM_{10} during different season are associated with differences in sampling days ($\text{PM}_{2.5}$ sampling were mostly happened during dust storm days). The standard $\text{Mg}^{2+}/\text{Na}^+$ ratio is 0.23. However in the present study the values found to be significantly lower than the standard values (Fig. 7). This could be associated with the large influx of sea salt aerosols, resulting in the loss of Mg^{2+} aerosols as suggested by Watanabe et al. (2010).

Correlation matrix analysis has been performed to find the source of co existence of different dominant ionic species (Table 2). A good correlation ($R=0.77$ to 0.87) between sulphate and nitrate in TSP, PM_{10} and $\text{PM}_{2.5}$, indicates, sources of similar origin, attributed to the co-emissions from their precursors viz. SO_4^{2-} and NO_x . Similarly higher correlation ($R=0.57$ to 0.78) between Ca and Mg also suggests their co existence from sources of crustal origin (Mouli et al. 2006). Good correlations were also observed between ion pairs such as Mg^{2+} and Cl^- , K^+ and NO_3^- , K^+ and SO_4^{2-} , Mg^{2+} and Na^+ , Na^+ and Cl^- , NH_4^+ and SO_4^{2-} , Ca^{2+} and Mg^{2+} , indicating common sources of origin. This high correlation between crustal ions and acidic ions suggests that the ionic composition were mainly contributed by terrestrial sources of similar origin, from soil dust as well as that originate from anthropogenic activities. The predominant source for the above combinations could be the reactions of the acids H_2SO_4 and HNO_3 with alkaline compounds rich in Ca, Mg, and K and NH_4 . From Table 2, it can be seen that NaCl , CaSO_4 , MgSO_4 , MgCl_2 , KNO_3 , HNO_3 , NH_4NO_3 , NH_4SO_4 and $(\text{NH}_4)_2\text{SO}_4$ are predominant species combinations over the site,

Table 2 Correlation matrix of ionic components of TSP, PM₁₀ (Red letters) and PM_{2.5} (Blue letters). Correlations significant at 95% confidence level are shown in bold letters and significant at 90% level are shown in italics

	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
F ⁻	1								
Cl ⁻	0.135 0.284 <i>0.597</i>	1							
NO ₃ ⁻	0.132 0.217 <i>0.138</i>	0.085 0.110 <i>0.499</i>	1						
SO ₄ ²⁻	0.058 <i>-0.013</i> -0.424	0.091 <i>0.078</i> <i>-0.121</i>	0.775 0.772 <i>0.317</i>	1					
Na ⁺	0.150 0.334 <i>0.231</i>	0.975 0.970 0.664	0.059 <i>0.081</i> 0.766	0.137 <i>0.093</i> 0.489	1				
NH ₄ ⁺	0.028 <i>-0.060</i> <i>-0.340</i>	-0.029 <i>-0.031</i> <i>-0.348</i>	0.870 0.860 <i>0.276</i>	0.886 0.936 0.770	-0.027 <i>-0.043</i> <i>0.135</i>	1			
K ⁺	0.181 <i>0.123</i> <i>-0.219</i>	0.378 0.296 <i>0.021</i>	0.739 0.749 0.510	0.845 0.871 0.931	0.395 0.311 0.598	0.737 0.770 0.788	1		
Mg ²⁺	<i>0.244</i> 0.410 <i>-0.006</i>	0.912 0.912 <i>0.200</i>	<i>0.241</i> <i>0.234</i> <i>0.282</i>	0.286 <i>0.233</i> 0.493	0.936 0.922 <i>0.390</i>	0.114 <i>0.088</i> <i>0.301</i>	0.567 0.460 0.570	1	
Ca ²⁺	0.393 0.407 <i>-0.156</i>	0.585 0.580 <i>0.298</i>	0.266 <i>0.207</i> <i>0.352</i>	0.291 <i>0.228</i> 0.581	0.615 0.563 0.547	0.113 <i>0.102</i> <i>0.188</i>	0.478 0.295 0.517	0.778 0.697 0.576	1

which may be formed in the atmosphere by the reaction between gaseous species and soil particles (Mouli et al. 2006).

Meteorological parameters have been correlated with mass fractions of TSP, PM₁₀, PM_{2.5} and its chemical compositions to find the possible influence of meteorology on chemical composition of TSP, PM₁₀ and PM_{2.5}. Significant positive correlations observed between sulphate mass and temperature indicates the release of sea salt sulphate fractions from adjacent oceanic areas due to high evaporation. The positive relations between humidity and various components in TSP and particulate matter (SO₄²⁻, NH₄⁺, K⁺, NO₃⁻) are associated with the relative humidity growth of these components. Positive correlation between chemical components and wind speed indicates the transport of components to the observational site by wind. The correlation analysis between chemical components and meteorological parameters are depicted in Table 3.

Table 3 Correlation between Meteorological parameters and TSP, PM₁₀ (Red letters) and PM_{2.5} (Blue letters). Correlations significant at 95% confidence level are shown in bold letters and significant at 90% level are shown in italics

Wind speed (m/s)				Temperature (°C)				Humidity (%)			
Wind speed	1										
Temp.	0.09				1						
Humidity	0.23				0.40				1		
Mass Concentration	0.21	0.06	-0.22	-0.24	-0.07	0.09	-0.09	0.08	0.42		
F ⁻	0.09	0.23	0.01	0.07	-0.22	-0.28	0.12	-0.12	-0.23		
Cl ⁻	0.59	0.57	0.11	-0.23	-0.17	0.24	-0.20	-0.17	-0.06		
NO ₃ ⁻	-0.04	0.05	-0.20	0.14	0.24	0.28	0.34	0.39	0.33		
SO ₄ ²⁻	0.01	0.05	0.06	0.20	0.33	0.51	0.38	0.43	0.48		
Na ⁺	0.59	0.59	0.00	-0.23	-0.17	0.65	-0.16	-0.13	0.36		
NH ₄ ⁺	-0.02	0.10	-0.16	0.23	0.35	0.17	0.33	0.41	0.41		
K ⁺	0.23	0.13	0.02	0.01	0.19	0.44	0.20	0.33	0.56		
Mg ²⁺	0.49	0.47	0.16	-0.27	-0.18	0.09	-0.15	-0.11	0.41		
Ca ²⁺	0.24	0.19	0.11	-0.25	-0.08	0.32	-0.20	-0.18	0.13		

3.3 Neutralization factors

Neutralization Factor (NF) has been estimated to find the neutralization capability of main basic components. The NF for NH₄⁺, Ca²⁺, Mg²⁺ and K⁺, which are major basic components has been estimated using equivalent concentrations of components as explained in Kulshrestha et al. (2003).

Anmyeon-do being an island site, a fraction of aerosol components could have been transported from adjacent oceans. Since marine alkaline components lacks potential neutralizing efficiency, non sea salt (nss) fractions have been calculated by taking Na⁺ as reference as follows,

$$nssX = X_{(insample)} - [X/Na_{(inSea)} * Na_{(insample)}]$$

Hence the NF values for major basic components, viz. Ca, NH₄, K and Mg has been estimated as,

$$NF(Ca) = nss Ca/NO_3 + nssSO_4; NF(NH_4) = NH_4/NO_3 + nssSO_4;$$

$$NF(Mg) = nss Mg/NO_3 + nssSO_4; NF(K+) = nss K + /NO_3 + nssSO_4$$

Neutralization factors (NF) for different cationic species are shown in Table 4. During the entire season, NH₄⁺ ion served as prominent neutralizing agent in TSP, PM₁₀ and

Table 4 Neutralization Factor values for Ca^{2+} , NH_4^+ , Mg^{2+} and K^+ in TSP, PM_{10} (Red letters) $\text{PM}_{2.5}$ (Blue letters) during different seasons

		NF Ca^{2+}	NF NH_4^+	NF Mg^{2+}	NF K^+
2003	Spring	0.186 0.101 0.071	0.408 0.449 0.347	0.019 0.016	0.033 0.046 0.122
	Summer	0.096 0.050 0.054	0.606 0.489 0.091	0.014 0.001	0.034 0.041 0.147
	Autumn	0.174 0.120 0.031	0.714 0.721 0.255	0.022 0.001	0.047 0.059 0.116
	Winter	0.119 0.125 0.088	0.579 0.704 0.452	0.019 0.024	0.057 0.070 0.169
2004	Spring	0.492 0.377 0.158	0.611 0.703 0.140	0.049 0.034	0.054 0.052 0.122
	Summer	0.072 0.063 0.046	0.982 1.035 0.343	0.009 0.006	0.035 0.043 0.106
	Autumn	0.172 0.172 0.056	0.915 0.967 0.192	0.026 0.022	0.048 0.052 0.127
	Winter	0.256 0.178 0.081	0.865 0.848 0.210	0.044 0.036	0.046 0.047 0.139

$\text{PM}_{2.5}$. The NF values for NH_4^+ ranged from 0.4 to 1.0 in TSP during different seasons. Higher NF values were observed during summer and autumn seasons. The NF values for NH_4^+ found to be higher for PM_{10} (0.45 to 1.1) compared to $\text{PM}_{2.5}$ (0.1 to 0.2), indicating higher neutralization of acidic components by coarse mode fractions than fine mode aerosols. The NF values for Ca^{2+} found to be 0.08 to 0.2 in different seasons. In general the NF values found to be in the order $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ for TSP and particulate matter in different seasons (Table 4), suggesting high neutralization of acidic factors by Ammonium in all seasons.

4 Summary

Aerosol chemical properties have been analyzed over a Global Atmosphere watch supersite, Anmyeon-do in South Korea, during 2003–2004 periods. Aerosol samplers

were operated to collect total suspended particulates (TSP), PM₁₀ and PM_{2.5} concentrations. TSP showed a significant seasonal variation with consistent higher values during spring season. Concentration of PM₁₀ also showed the same trend as of TSP with maximum value during spring and minimum during summer. PM_{2.5} showed an enhancement during summer, which could be associated with influx of fine mode aerosols from adjacent oceans. The back trajectory analysis revealed the air mass tracks during different seasons, which were found to be directed from west, north-west directions during different seasons. The air mass tracks were observed from south west during summer, which might bring fine mode sea salt aerosols associated with the Changma front. Chemical composition analysis of TSP, PM₁₀ and PM_{2.5} showed a dominant presence of acidic fraction, especially contributed by sulfates and nitrates during different seasons. Enhanced presence of Ca²⁺ was observed on sand storm days during spring and winter, suggesting Ca²⁺ is a major component in desert dust. The high correlation obtained on matrix analysis between crustal ions and acidic ions suggests that the ionic composition was influenced by terrestrial sources of similar origin. Meteorological parameters such as wind speed and Relative humidity are found to be major factors influencing aerosol chemical composition. The neutralization factors has been estimated to find the extend of neutralization by basic components, and found to have highest value for NH₄⁺, varying between 0.4 and 1.1, indicating significant neutralization of acidic components over the region by NH₄⁺ in different seasons.

Acknowledgements This work is supported by National Research Foundation of Korea (NRF) through a grant provided by the Korean Ministry of Education, Science & Technology (MEST) in 2011 (No. K20607010000). The aerosol chemical datasets maintained in Anmyeon-do GAW center used in this study is gratefully acknowledged. Back trajectories obtained from HYSPLIT model are acknowledged with thanks. We thank two anonymous referees for their kind suggestions.

References

- Al-Khashman, O.A.: Ionic composition of wet precipitation in the Petra Region, Jordan. *Atmos. Res.* **78**, 1–12 (2005)
- Chatterjee, A., Adak, A., Singh, A.K., Srivastava, M.K., Ghosh, S.K., Tiwari, S., Devara, P.C., Raha, S.: Aerosol chemistry over a high altitude station at Northeastern Himalayas, India. *PLoS ONE*. **5**, 1–20 (2010)
- Cooper, J.A.: Environmental impact of residential wood combustion emissions and its implications. *J. Air Pollut. Control Assoc.* **30**, 855–861 (1980)
- Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.P., Yang, D.G., Chu, C.C.: Characterization of chemical species in PM_{2.5} and PM₁₀ aerosols in suburban and rural sites of central Taiwan. *Atmos. Environ.* **234**, 203–212 (1999)
- Gautam, R., Liu, Z., Singh, R.P., Hsu, N.C.: Two contrasting dust-dominant periods over India observed from MODIS and CALIPSO. *Geophys. Res. Lett.* **36**, L06813 (2009)
- Kim, B.G., Park, S.U.: Transport and evolution of a winter-time Yellow sand observed in Korea. *Atmos. Environ.* **35**, 3191–3201 (2001)
- Kim, K.W., Kim, Y.J., Oh, S.J.: Visibility important during Yellow Sand periods in the urban atmosphere of Kwangju, Korea. *Atmos. Environ.* **35**, 5157–5167 (2001)
- Kleinman, M.T., Tomezy, C., Leaderer, B.P., Tanner, R.L.: Inorganic nitrogen compounds in New York City air. *Ann. N. Y. Acad. Sci.* **322**, 115–123 (1979)
- Ko, H.J., Kim, W.H., Lee, M.Y., Song, J.M., Kang, C.H., Kim, Y.P.: Variation of TSP Compositions in Accordance with the Pathways of Inflowing Air Mass at Jeju Island (in Korean). *J. KOSAE.* **27**(3), 347–357 (2011)
- Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R., Vairamani, M.: Chemical characteristics of rainwater at an urban site of south-central India. *Atmos. Environ.* **37**, 3019–3026 (2003)

- Mori, I., Nishikawa, M., Iwasaka, Y.: Chemical reaction during the coagulation of ammonium sulphate and mineral particles in the atmosphere. *Sci. Tot. Environ.* **224**, 87–91 (1998)
- Mouli, P.C., Mohan, S.V., Reddy, S.J.: Chemical composition of atmospheric aerosol (PM10) at a semi-arid urban site: Influence of terrestrial sources. *Environ. Monit. Assess.* **117**, 291–305 (2006)
- Panicker, A.S., Pandithurai, G., Safai, P.D., Dipu, S., Lee, D.I.: On the contribution of black carbon to the composite aerosol radiative forcing over an urban environment. *Atmos. Environ.* **44**, 3066–3070 (2010a)
- Panicker, A.S., Pandithurai, G., Dipu, S.: Aerosol indirect effect during successive contrasting monsoon years over Indian sub continent: using MODIS data. *Atmos. Environ.* **44**, 1937–1943 (2010b)
- Rao, P.S.P., Momin, G.A., Safai, P.D., Ali, K., Naik, M.S., Pillai, A.G.: Aerosol and trace gas studies at Pune during INDOEX IFP-99. *Curr. Sci.* **80**, 105–109 (2001)
- Safai, P.D., Rao, P.S.P., Momin, G.A., Ali, K., Tiwari, S., Naik, M.S., Kuniyal, J.C.: Chemical composition of size-separated aerosols at two rural locations in the Himalayan region. *Indian J. Radio Space Phys.* **30**, 270–277 (2002)
- Safai, P.D., Rao, P.S.P., Momin, G.A., Ali, K., Chate, D.M., Praveen, P.S., Devara, P.C.S.: Variation in the chemistry of aerosols in two different winter seasons at Pune, Sinhadad. *India. Aerosol Air Qual. Res.* **5**, 115–126 (2005)
- Seigneur, C., Saxena, P.: A theoretical investigation of sulfate formation in clouds. *Atmos. Environ.* **22**, 101–115 (1988)
- Seinfeld, J.H., Pandis, S.N.: *Atmospheric chemistry and physics*. Wiley, New York (1998)
- Twomey, S.: The influence of pollution on the shortwave albedo of clouds. *J. Atmos. Sci.* **34**, 1149–1152 (1977)
- Uematsu, M., Hattori, H., Nakamura, T., Narita, Y., Jung, J., Matsumoto, K., Nakaguchi, Y., Kumar, M.D.: Atmospheric transport and deposition of anthropogenic substances from the Asia to the East China Sea. *Mar. Chem.* **120**, 108–115 (2010)
- Wang, H., Han, G.: Chemical composition of rainwater and anthropogenic influences in Chengdu. *Southwest China. Atmos. Res.* **99**, 190–196 (2011)
- Wang, Y., Zhuang, G., Sun, Y., An, Z.: The variation of characteristics and formation mechanisms of aerosol in dust, haze, clear days in Beijing. *Atmos. Environ.* **40**, 6579–6591 (2006)
- Watanabe, K., Kasuga, H., Yamada, Y., Kawakami, T.: Size distributions of aerosol number concentrations and water-soluble constituents in Toyama, Japan: a comparison of the measurements during Aisan dust period with non-dust period. *Atmos. Res.* **82**, 719–727 (2006)
- Watanabe, K., Honoki, H., Iwai, A., Tomatsu, A., Noritake, K., Miyashita, N., Yamada, K., Kawamura, H., Aoki, K.: Chemical characteristics of fog water at Mt. Tateyama, near the coast of the Japan Sea in Central Japan. *Water, Air, Soil Pollut.* **211**, 379–393 (2010)
- WMO/GAW: Manual for the GAW precipitation chemistry programme—Guidelines, data quality objectives and standard operating procedures. WMO/GAW precipitation chemistry science advisory group. 36–50 (2004)
- Zang, X.Y., Gong, S.L., Arimoto, R., Shen, Z.X., Mei, F.M., Wnag, D., Cheng, Y.: Characterization and temporal variation of asian dust aerosol from site in the Northern Chinese Deserts. *J. Atmos. Chem* **44**, 241–257 (2003)
- Zhou, Y., Wang, T., Gao, X., Xue, L., Wang, X., Wang, Z., Gao, J., Zhang, Q., Wnag, W.: Continuous observations of water-soluble ions in PM2.5 at Mount Tai (1534 ma.s.l.) in central-eastern China. *J. Atmos. Chem.* **64**, 107–127 (2009)