Atmospheric Research 94 (2009) 345–355

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Asian Dust effects on Total Suspended Particulate (TSP) compositions at Gosan in Jeju Island, Korea

Chang-Hee Kang, Won-Hyung Kim, Hee-Jung Ko, Sang-Bum Hong *

Department of Chemistry and Research Institute for Basic Sciences, Jeju National University, 1 Aradong, Jeju 690-756, South Korea

ARTICLE INFO

Article history:
Received 8 July 2008
Received in revised form 18 June 2009
Accepted 24 June 2009

Keywords:
Asian Dust
Aerosol composition
Ion balance
Regression analysis
Total Suspended Particulate

ABSTRACT

The compositions of TSP between AD and NAD storm periods were compared to study their long-term variations and chemical characteristics. TSP samples were collected at Gosan site in Jeju Island of Korea from February to May of 1992–2004. The major ionic and elemental species of TSP aerosols were analyzed. During AD periods, the concentrations of crust components (nss-Ca^{2+}, Al, Fe, Ca, Mg, Ba, Sr, Ti) increased remarkably, and the concentrations of anthropogenic components (nss-SO_4^{2-}, NO_3^-, S, Zn, Pb, Cr, Ni, Cd), with the exception of NH_4^+, increased weakly. The concentration ratios of all major components between AD and NAD periods showed ranges from 1.2 to 8.5, except for NH_4^+. The slope of the linear regression indicated that the contribution of CO_3^{2-} may have comprised up to 17% of the total anions. Our results suggested that the AD storm greatly influenced TSP compositions. Linear regression analyses indicated that NH_4^+ was not correlated with NO_3^-, but highly correlated with nss-SO_4^{2-} during both periods. The nss-SO_4^{2-} was also correlated with NH_4^+, K^+, nss-Mg^{2+}, and nss-Ca^{2+} during both periods. Interestingly, NO_3^- was associated with nss-Ca^{2+} and nss-Mg^{2+} during AD periods. Of the metal elements, Fe, Ca, Mg, Ti, Mn, Ba, Sr, V, and Co were highly correlated with Al during both periods, signifying that these metals were mostly originated from soils.

1. Introduction

The substantial amounts of gaseous and particulate air pollutants are emitted from East Asian nations due to the high population size and energy consumption of the region (Arndt et al., 1998). This is especially true of northeastern Asia, including the countries of Korea, China, and Japan. This region is characterized by high emissions of both anthropogenic and natural ambient trace species of pollutants (Streets et al., 2003). Of the natural emission sources, Asian Dust (AD) is common during late winter and spring seasons. AD occurs in arid regions during high-speed surface wind conditions (Duce et al., 1980). Under the favorable conditions, significant amounts of AD can be transported with the westerly wind from China continents to Korea (Park and Cho, 1998), Japan (Ishikawa et al., 1998), Hawaii (Perry et al., 1999), and even to western sections of the U.S. mainland (Jaffe et al., 1999, 2003).

An analysis of aerosol size distribution during AD period in Korea showed that the particles with the range of 1.35–10 µm size, especially in 2–3 µm ranges, increased due to the inclusion of mineral components originated from AD source regions (Chun et al., 2001a). The optical depth of the atmosphere was also much thicker and was characterized by larger particles during heavy dust storms compared to non-dust days (Chun et al., 2001b).

Previous studies have reported that high concentrations of mineral elements and high levels of anthropogenic species, such as sulfate and nitrate, were observed in the outflow from continental Asia (Talbot et al., 1997). These studies suggested that the interaction of AD with various kinds of pollutants in urban sites, such as black carbon, toxic materials, and acidic gases, may change their chemical and physical characteristics. These are important issues having been investigated in the field of atmospheric research, in order to clarify the influences of AD on regional air quality and the global environment. To address these issues, several routine and intensive measurement

* Corresponding author. Present address: Korea Polar Research Institute, KORDI, 7-50 Songdodong, Yeonsugu Incheon 406-840, South Korea. Tel.: +82 64 754 3545; fax: +82 64 756 3561.
E-mail address: lighthsb@Jejunu.ac.kr (S.-B. Hong).

0169-8095/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.atmosres.2009.06.013

studies, including PEM-West A and B, ACE-Asia, and ABC, have been conducted at Gosan on Jeju Island, Korea, since 1991 (Arimoto et al., 1996; Chen et al., 1997; Lee et al., 2001; Huebert et al., 2003). The Gosan site is located at the western edge of Jeju Island, which is downwind from the westerly of northeast Asia. Therefore, this site is an important background area for which the characteristics of air pollutants and air masses transported from northeast Asia, specifically from China continent (see Fig. 1), can be effectively evaluated.

The objective of this study was to intensively investigate AD effects on the chemical characteristics of Total Suspended Particulate (TSP) with long-term measurement data during 1992–2004. Ion balances of water-soluble species in TSP during AD and non-AD (NAD) periods were determined and the existence of CO_3^{2-} associated compounds in TSP during the AD period were discussed. The chemical compositions between AD and NAD periods were compared in order to clarify AD effects on the TSP aerosols at Gosan site in Korea during spring seasons. The correlation characteristics *of* TSP species between AD and NAD periods were also compared in order to investigate their sources and associations between the species.

2. Experimental

2.1. Collection of aerosol samples

Field measurements were taken at the Gosan site in Jeju Island, Korea (33° 17′ N, 126° 10′ E; Fig. 1). The characteristics of the measurement site were described in detail in previous studies (Arimoto et al., 1996; Chen et al., 1997; Kim et al., 1998; Park et al., 2003, 2004).

A high-volume tape sampler (Kimoto Electric Co., Model 195A) with roll-type PTFE filters (Sumitomo Electric, 100 mm × 10 m) was equipped in a temperature-controlled trailer. The inlet was placed on the roof of the trailer, approximately 6 m above the ground. The flow rate for aerosol samplings was about 170 Lpm. A total of 1927 TSP aerosol filters had been collected from March 1992 to December 2004. Most of the samples were collected for a 24-hour basis, but some were collected over 6- or 12-hour intervals, and all data presented in this study were averaged to 24-hour basis. Only 790 of the samples, taken between the months of February and May of AD periods, were selected for this study. Of these sampling days, AD events occurred for 49 days, and the others were 741 days of NAD events. These AD events were chosen from the weather reports according to the Korea Meteorological Organization.

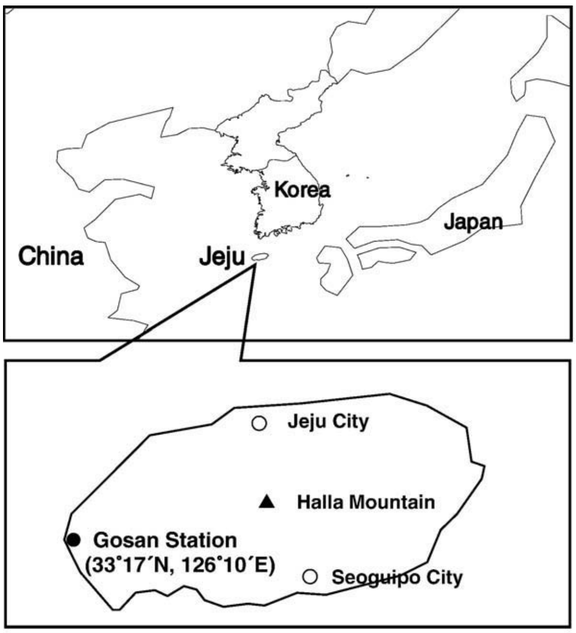

Fig. 1. Map of Gosan measurement site.

2.2. Analysis of aerosol samples

The aerosol-containing filters (75 mm diameter) were divided into two portions; one portion was used for the analysis of ionic species and the other for the analysis of sulfur (S) and metal elements. Among the ion species analyzed, NH_4^+ was analyzed using the indophenol method with UV–visible spectrophotometer (Kontron, UVIKON 860), and Na^+, K^+, Ca^{2+}, and Mg^{2+} were analyzed using atomic absorption spectroscopy (GBC, Avanta-P) for the samples taken between 1992 and 2000. For the samples taken after 2000, these ions were analyzed by ion chromatography (Dionex DX-500 and Metrohm Modula IC), along with the IonPac CS12 column and the Metrosep Cation 1-2-6 column for cations. For anions, IC method was used during total period with different analytical columns such as the IonPac AS4A-SC column and the Metrosep A SUPP 4 column. An inductively coupled plasma (ICP-AES) spectrometer (Jobin-Yvon Emission Instruments, Model JY 38S till 1997, and Thermo Jarrel Ash, IRIS-DUO system after 1998) was used for the analysis of sulfur and metal elements. The operation conditions were 40.68 MHz RF/1150 W with an outer air flow rate of 16.0 L min^{-1}, an inner air flow rate of 0.5 L min^{-1}, and simultaneous mode. As a quality assurance/quality control (QA/QC), the data were excluded if rainfall exceeded 3 mm or the percent imbalance was >30% (Park et al., 2004) and, using these criteria, 23.2% of the samples were excluded.

3. Results and discussion

3.1. Comparison of TSP compositions between AD and NAD periods

The concentrations and their ratios of TSP aerosol species for AD and NAD periods are shown in Fig. 2 and Table 1. The mean concentrations of the aerosol components during AD periods were in order from the largest: nss-SO_4^{2-} > NO_3^- > Cl^- > nss-Ca^{2+} > Na^+ > NH_4^+ > K^+ > Mg^{2+} for the ionic species, and Al > Ca > Fe > S > Mg > K > Ti > Mn > Zn > Pb > Ba > V > Sr > Ni > Cu ≈ Cr ≈ Co ≈ Cd ≈ Mo for the elemental species. During NAD periods, the orders of the mean concentrations were: nss-SO_4^{2-} > NO_3^- > Na^+ > Cl^- > NH_4^+ > nss-Ca^{2+} > K^+ > Mg^{2+} for the ionic species, and S > K > Ca > Al > Fe > Mg > Zn > Pb > Ti > Mn > V > Ba > Ni > Cu > Sr ≈ Cr ≈ Co ≈ Cd ≈ Mo for the elemental species. Of the elemental species, the concentrations of S, Al, Fe, and Ca showed high values comparably, and they were as 10–100 times high as the levels of Zn, Cr, Pb, Ni, and Cu.

The nss-SO_4^{2-} showed the highest concentrations among the water-soluble species, and were composed of 33% and 45%

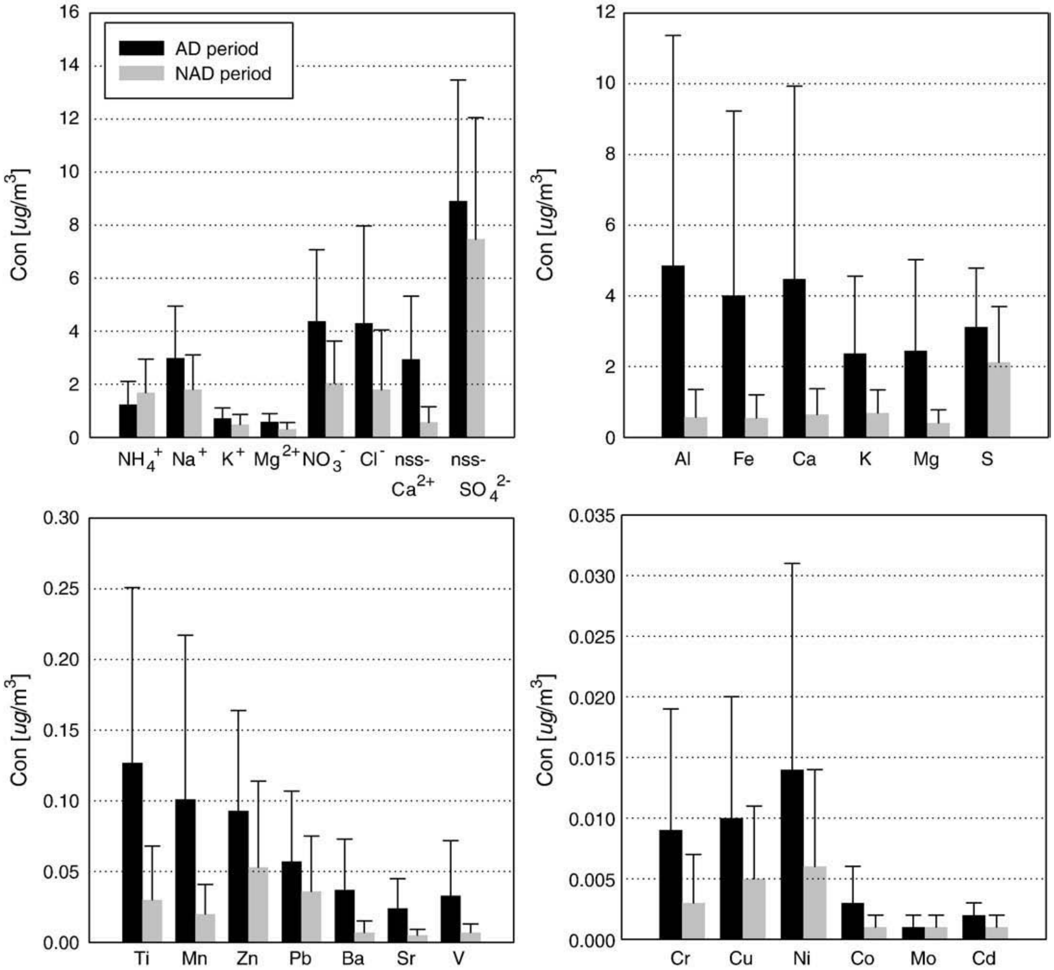

Fig. 2. Concentrations (μg/m^3) of TSP components during Asian Dust (AD) and Non-Asian Dust (NAD) periods, measured at Gosan site from February to May of 1992–2004. (arithmetic average value with 1 standard deviation, [nss-Ca^{2+}] = [Ca^{2+}] − 0.041 [Na^+], [nss-SO_4^{2-}] = [SO_4^{2-}] − 0.251 [Na^+]).

in the total water-soluble species during AD and NAD periods, respectively. The nss-Ca^{2+}, one of typical components of soil particles, occupied 11% and 3% of the whole water-soluble species during AD and NAD periods, respectively. The concentrations of the species typically derived from the soil, such as Al, Fe, and Ca, increased remarkably during AD periods. These components were composed roughly of 54% of the total elemental species. Sulfur, primarily derived from anthropogenic sources, has occupied 13% of the AD particles. However, the NAD particles showed a quite different composition pattern, as 24% for Al, Fe, Ca, and 35% for S.

The concentration ratios of the ionic species in TSP between AD and NAD periods have been compared to investigate the effects of the AD storm on the chemical compositions in TSP (see Table 1). Of the ionic species, the highest ratio was 5.2 for nss-Ca^{2+}, indicating the evidence of the AD storms. The concentration ratios of NO_3^-, nss-SO_4^{2-}, and NH_4^+, which are formed secondarily in an atmospheric environment, were 2.1, 1.2, and 0.7, respectively. Interestingly, the concentrations of NH_4^+ were slightly lower during AD periods than those during NAD periods. Previous studies have shown that NH_4^+ is closely associated with nss-SO_4^{2-} and NO_3^- in the fine fraction of

Table 1
Concentration ratios of TSP components between Asian Dust (AD) and Non-Asian Dust (NAD) periods, measured at Gosan site from February to May of 1992–2004.

Species	NH_4^+	Na^+	K^+	Mg^{2+}	NO_3^-	Cl^-	nss-Ca^{2+} [a]	nss-SO_4^{2-} [b]	Al	Fe	Ca
AD/NAD	0.7	1.7	1.5	1.9	2.1	2.4	5.2	1.2	8.5	7.3	7.0
Species	K	Mg	S	Ti	Mn	Ba	Sr	Zn	V	Cr	Pb
AD/NAD	3.5	6.0	1.5	4.2	5.2	5.2	4.8	1.7	4.5	3.1	1.6
Species	Cu	Ni	Co	Mo							
AD/NAD	2.0	2.5	4.4	1.0							

[a] Non-sea-salt–Ca^{2+} = Ca^{2+} − 0.041 [Na^+].
[b] Non-sea-salt–SO_4^{2-} = SO_4^{2-} − 0.251 [Na^+].

aerosols, but when a gaseous sulfur and nitrogen oxides react on the surface of dust particles, nss-SO_4^{2-} and NO_3^- might be associated with alkaline components of dust particles such as Ca^{2+} and Mg^{2+} (Park et al., 2003). Therefore, the role of NH_3, as a neutralizer of acidic species, could be decreased due to a relatively excessive presence of such alkaline soil species during AD periods, especially in the mode of 2–3 µm particles. Consequently, it might be reasoned that the concentrations of NH_4^+ in TSP decreased during AD periods. Meanwhile, the concentrations of Cl^- originated from a sea-salt have shown to increase by 2.4 times during AD periods. This may be ascribed to the absorption of gaseous HCl released from sea-salts onto dust particles (Zhang and Iwasaka, 2001; Sullivan et al., 2007).

The concentration ratios (AD/NAD) of Al, Fe, Ca, Mg, Mn, and Ba, which are mainly from a soil (Taylor and McLennan, 1985), were over 5.2, comparable to those of nss-Ca^{2+}. On the other hand, the concentration ratios of S, Zn, Pb, Mo, and Cd, mainly from anthropogenic sources, had a range from 1.0 to 1.7. These results suggest that the soil-sourced species are much more contributive to AD particles compared to the anthropogenic species. A one-way analysis of variance (ANOVA; $p=0.05$) showed that the mean values of the species during AD and NAD periods were significantly different, with the exception for Mo. That is, as expected, the AD storm affects most of the components in TSP. Our results have verified that the concentrations of all species, except only NH_4^+ and Mo, have increased during AD periods.

Our results are compared to those of Park et al. (2003) and presented in Fig. 3. The AD/NAD concentration ratios of soluble species in TSP were very similar in both studies. The ratios of the anthropogenic species, including Ti, Zn, Pb, Cu, Ni, and Cd, were relatively similar, but interestingly those of the soil-sourced species, such as Al, Fe, Ca, Mn, V, and Cr, showed quite different result. It indicates that the soil-sourced species are more variable by the bias of AD events. Yearly variations in the concentration ratios of the elemental species throughout the entire measurement period are illustrated in Fig. 4. The results indicated that the ratios of soil-derived species increased remarkably during AD periods in 1998 and 2002. These yearly fluctuations for the soil-derived species were dependent on the extent of the AD storms, and likely explained the differences between our study and that of Park et al. (2003).

3.2. Ion balances of water-soluble species

The ion balances of water-soluble species in TSP during AD and NAD periods have been determined and are presented in Fig. 5. The sum of cationic equivalent concentrations should be equal to the sum of anionic equivalent concentrations if all water-soluble ions were analyzed. Therefore, a comparison of the sums of equivalent concentrations of cations and anions validates the analysis of the data. Our results indicated that the anions were balanced by up to 102% of the cations during NAD periods ($y=1.02x+0.00$, $r^2=0.94$). However, the slope of the linear regression was only 0.82 ($r^2=0.92$) for the AD periods, suggesting that some anions were not determined.

Fig. 6 shows the linear regression results between $[NH_4^+]_{eq}+[K^+]_{eq}+[\text{nss-}Ca^{2+}]_{eq}+[\text{nss-}Mg^{2+}]_{eq}$ and $[\text{nss-}SO_4^{2-}]_{eq}+[NO_3^-]_{eq}$. The species originated mostly from sea-salt compounds were excluded. During NAD periods, the slope was 1.08

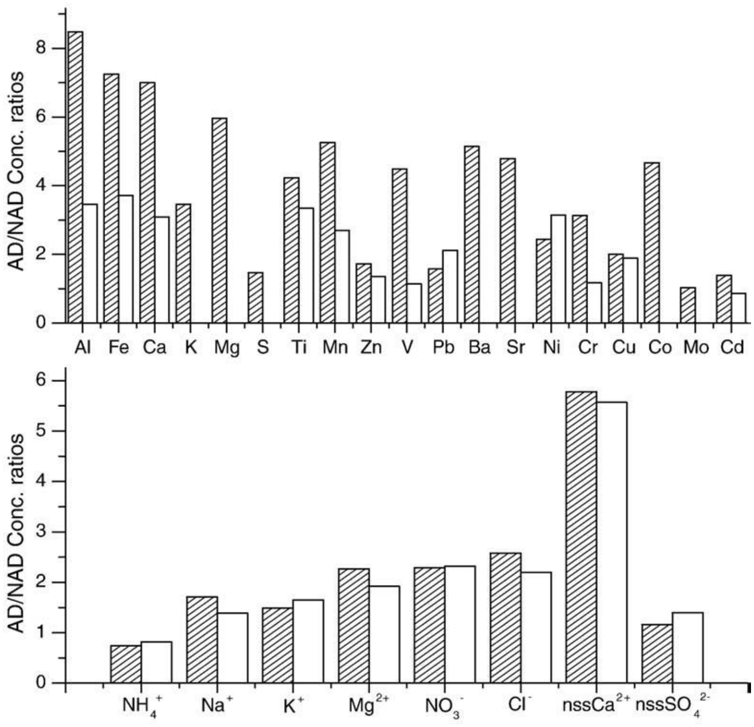

Fig. 3. Concentration ratios of major ionic species and metal components in TSP (▨, this study; □, Park et al., 2003. AD/NAD indicates the concentration ratios between Asian Dust and Non-Asian Dust periods).

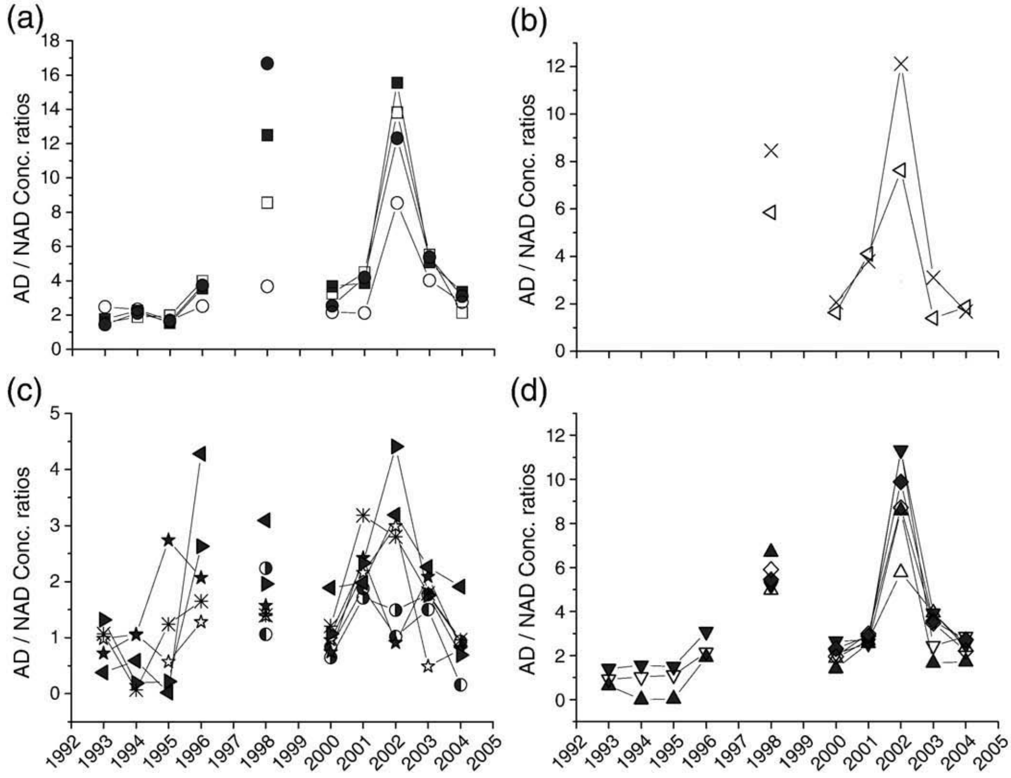

Fig. 4. The yearly variations of AD/NAD concentration ratios of (a) Al, Ca, Fe, Ti, (b) Mg, K, (c) S, Pb, Cd, Zn, Cu, Ni, Mo, and (d) Cr, Mn, V, Ba, Sr, Co, in TSP (■, Al; ●, Ca; □, Fe; ○, Ti; ×, Mg; ◁, K; ◑, S; ★, Pb; ☆, Cd; *, Zn; ►, Cu; ◄, Ni; ◐, Mo; ▲, Cr; ▼, Mn; ▽ V ; ♦, Ba; ◇, Sr; △, Co).

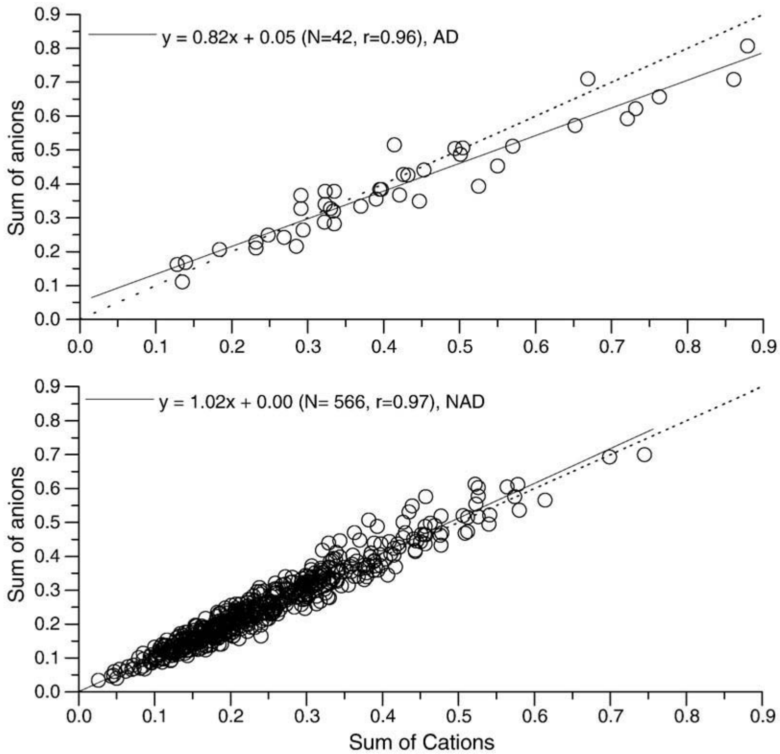

Fig. 5. Ion balance of water-soluble ionic species in TSP during Asian Dust and Non-Asian Dust periods.

and it showed high correlation results ($r = 0.93$), indicating that the acidic anions were almost neutralized by the basic cations. However, during AD periods, the slope was 0.77 ($r = 0.85$), suggesting that the sum of cationic equivalent concentrations were evidently larger than the sum of anionic equivalent concentrations.

Previous studies reported that the ion balance between the sums of cationic and anionic equivalent concentrations did not show a good correlation due to a relatively large excess of cations during AD events. This might be reasoned for the omission of a CO_3^{2-} measurement in the analytical process (Lee et al., 2003; Maxwell-Meier et al., 2004). The calcite has been known as a major compound in Asian mineral dust particles (Song and Carmichael, 1999, 2001; Cao et al., 2005; Chen et al., 2008).

Therefore, in this study, the estimated carbonate ion concentration ($[CO_3^{2-}]_{estimated}$) was calculated, because it was regarded as the ionic imbalance which is the difference between the sum of cationic equivalent concentrations and the sum of anionic equivalent concentrations. When $[CO_3^{2-}]_{estimated}$ was included in the regression analyses, the slope was 0.93 and the correlation was high ($r = 0.92$) for the AD periods (see Fig. 6). It is assumed that the salt compounds associating with CO_3^{2-}, an anion pair, may play an important role in the ion balance. In the result of this study, CO_3^{2-} contributed up to 17% of the sum of anionic equivalent concentrations. On the other hand, if those of over 30% among the ionic imbalances which are the differences between the sums of cationic and anionic equivalent concentrations are considered, the contribution of CO_3^{2-} can increase up to 32% as the maximum estimate. It could be assumed that CO_3^{2-} might be in the range of 17~ 32% of the sum of anionic equivalent concentrations. Consequently, more successful analysis of CO_3^{2-} would be required for better result of the comparable ion balance of water-soluble species in TSP for the AD periods.

3.3. Correlation between TSP aerosol species

Linear regression analyses have been carried out to find the source origins and the combinations of TSP species during AD and NAD periods. The regression method is occasionally used to investigate not only the associations between the species but also their composition ratios of TSP species. However, if only the concentration ratios of major species are included, it may be difficult to justify their associations. It has been reported that the correlation and molar ratio analyses are carried out between the ionic species in order to guess salt forms and sources of ion species in fine particles (Song et al., 2005).

Table 2 summarizes the results of the linear regression analyses of TSP elements against Al, which is a representative of soils. Al was correlated to Fe, Ca, Mg, Ti, Mn, Ba, Sr, V, and Co, and their correlation slopes between AD and NAD periods were similar. These results indicated that these elements were mainly derived from the soil because the concentration ratios between correlated species were similar during both AD and NAD periods. K, Cr, and Ni were interestingly well correlated with Al during AD periods, but had weak correlations during NAD periods, explaining that these metal elements were accompanied with AD particles and influenced into the air quality at the Gosan area. Al was not correlated with S, Zn, Pb, Cu, Mo, and Cd in both AD and NAD periods, indicating that

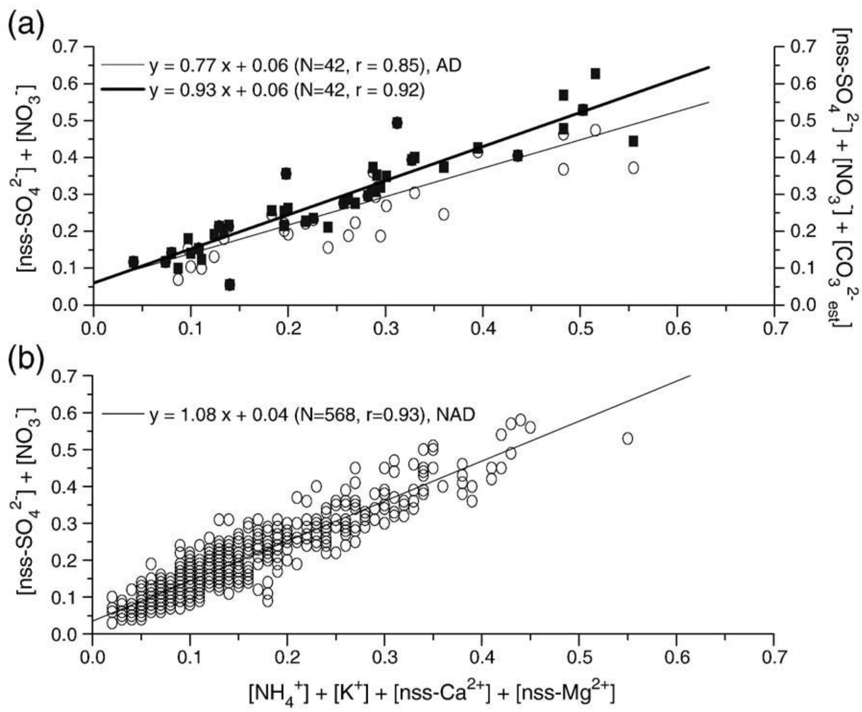

Fig. 6. Linear regression fits of $[NH_4^+] + [K^+] + [nss\text{-}Ca^{2+}] + [nss\text{-}Mg^{2+}]$, $[nss\text{-}SO_4^{2-}] + [NO_3^-]$, and $[nss\text{-}SO_4^{2-}] + [NO_3^-] + [CO_3^{2-}]_{estimated}$ in TSP during (a) Non-Asian Dust periods and (b) Asian Dust periods.

Table 2
Linear regression fits of TSP elements against Al during Asian Dust (AD) and Non-Asian Dust (NAD) periods from February to May of 1992–2004.

Species	AD			NAD		
	Slope	Intercept [a]	r^2	Slope	Intercept [a]	r^2
Fe	0.756 ± 0.042	337.4 ± 340.8	0.89	0.777 ± 0.017	108.2 ± 16.5	0.86
Ca	0.806 ± 0.036	558.7 ± 286.6	0.93	0.806 ± 0.027	177.9 ± 26.2	0.73
K	0.281 ± 0.024	679.2 ± 218.3	0.82	0.339 ± 0.044	466.7 ± 48.2	0.21
Mg	0.347 ± 0.022	353.4 ± 202.3	0.90	0.360 ± 0.015	176.8 ± 16.4	0.72
S	0.111 ± 0.0381	2447.8 ± 350.0	0.22	0.919 ± 0.104	1521.0 ± 113.3	0.26
Ti	0.017 ± 0.001	45.5 ± 11.5	0.78	0.033 ± 0.002	11.9 ± 1.9	0.45
Mn	0.017 ± 0.0008	17.4 ± 6.3	0.93	0.023 ± 0.001	6.2 ± 0.7	0.77
Ba	0.0049 ± 0.0002	7.3 ± 1.9	0.95	0.0072 ± 0.0003	2.4 ± 0.4	0.67
Sr	0.0026 ± 0.0002	7.7 ± 2.3	0.79	0.0036 ± 0.0002	2.5 ± 0.2	0.53
Zn	0.0048 ± 0.0015	69.6 ± 12.4	0.20	0.016 ± 0.0042	44.4 ± 4.1	0.04
V	0.0055 ± 0.0003	5.7 ± 2.6	0.88	0.006 ± 0.0003	3.9 ± 0.3	0.56
Cr	0.0015 ± 0.00008	2.3 ± 0.7	0.89	0.002 ± 0.0003	1.9 ± 0.3	0.14
Pb	0.0002 ± 0.00122	55.6 ± 9.8	0.00	0.019 ± 0.003	24.9 ± 2.5	0.14
Cu	0.0008 ± 0.0002	6.1 ± 1.8	0.23	0.0011 ± 0.0004	4.2 ± 0.4	0.02
Ni	0.0007 ± 0.0001	6.5 ± 1.0	0.51	0.0033 ± 0.0006	4.0 ± 0.5	0.10
Co	0.0004 ± 0.00003	0.6 ± 0.3	0.83	0.0005 ± 0.00004	0.3 ± 0.0	0.49
Mo	0.0001 ± 0.00002	1.1 ± 0.2	0.00	0.0002 ± 0.00005	1.0 ± 0.1	0.04
Cd	0.0001 ± 0.00002	1.1 ± 0.2	0.35	0.0001 ± 0.00007	1.2 ± 0.1	0.01

[a] The unit of intercept values is ng/m^3.

these elements might be originated from the other sources, probably from industrial activities as well as anthropogenic sources.

The linear regression analyses between Na^+ and Cl^- showed the slopes of 1.02 and 1.05 respectively during AD and NAD periods, and indicated a high correlation between these two ions (the correlation coefficients were over 0.85; see Fig. 7). Their concentration ratios in TSP are expected to be similar to those in sea-salt due to the influence of sea-salt spray from the marine area on the Gosan site. However, the slopes from the linear regressions were somewhat lower than those in sea-salt during both periods (the theoretical molar ratio of Cl^-/Na^+ is 1.16). Fig. 8 illustrates the scattergrams for nss-SO_4^{2-} and Cl^-, showing negative relationships (AD periods; $r = -0.16$, NAD periods; $r = -0.25$) between the two species. Especially, in the method of correlation analyses, the correlation is significant at the 0.01 level (2-tailed) during NAD periods and this relationship may be ascribed to the reactions of acidic gases with sea-salt particles, resulting in chlorine loss. The gaseous HCl is known to be liberated through the reaction of NaCl with surrounding acidic gases and H_2SO_4 incorporated into marine aerosols (Shimohara et al., 2001; Kim et al., 1993a,b). Park et al. also reported that the negative value of the correlation coefficient between Cl^- and nss-SO_4^{2-} ($r = -0.21$) at Gosan site suggested that acidic particles caused chlorine loss (2004).

Fig. 9 shows the linear regression analyses between nss-SO_4^{2-} and cationic species NH_4^+, K^+, nss-Mg^{2+}, and nss-Ca^{2+}. NH_4^+ was generally correlated with nss-SO_4^{2-} ($r = 0.62$ and 0.89), but the slopes were 0.32 and 0.64 during AD and NAD periods, respectively. Therefore, the neutralizing contributions of NH_4^+

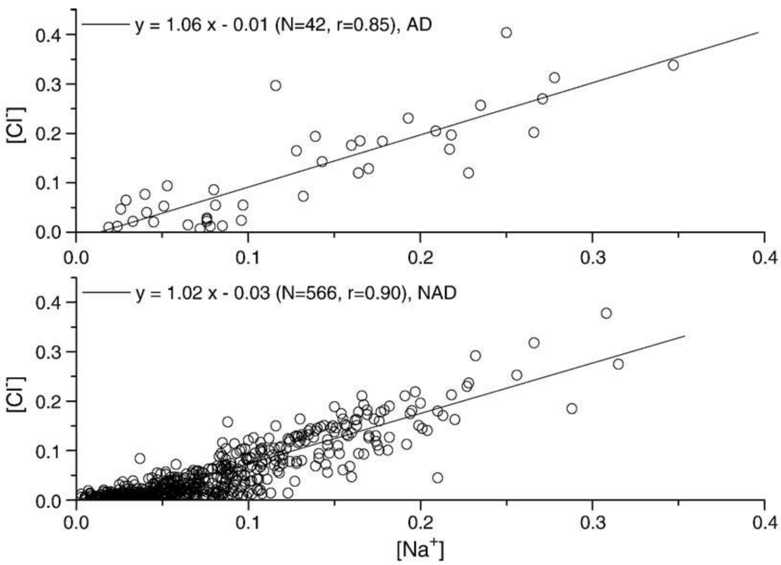

Fig. 7. Liner regression fits of [Na^+] and [Cl^-] in TSP during Asian Dust and Non-Asian Dust periods.

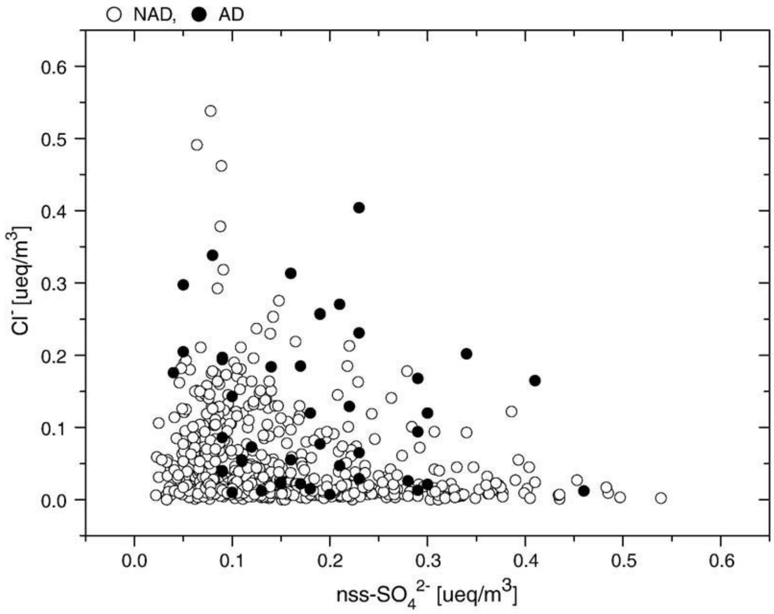

Fig. 8. Scattergrams of [Cl^-] and [nss-SO_4^{2-}] in TSP during Asian Dust and Non-Asian Dust periods.

were greater during NAD periods. A previous study reported the correlation coefficient (r) of 0.87 between NH_4^+ and nss-SO_4^{2-} in the fine mode aerosols, meaning that NH_4^+ was associated mostly with nss-SO_4^{2-} and partially combined with NO_3^- (Park et al., 2004). It was expected that the remaining nss-SO_4^{2-} was combined with other basic metallic cations in the coarse mode

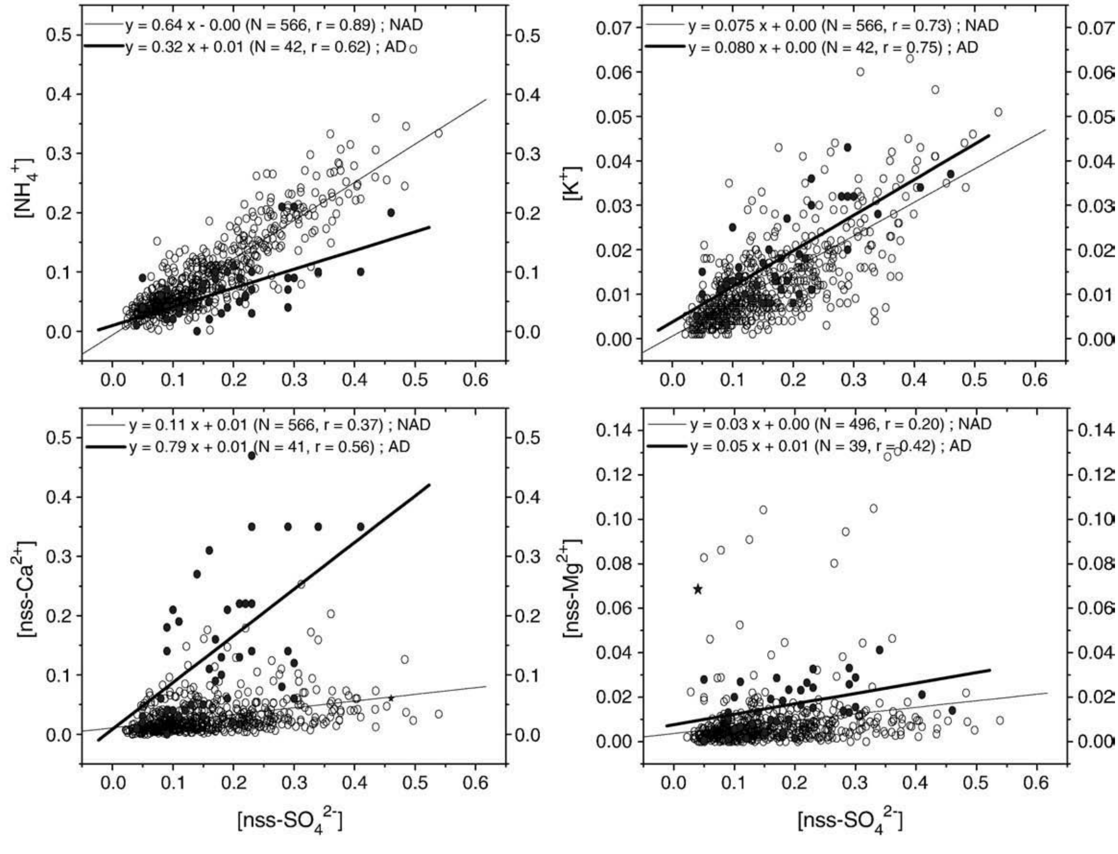

Fig. 9. Linear regression fits of [NH_4^+], [K^+], [nss-Ca^{2+}], and [nss-Mg^{2+}] against [nss-SO_4^{2-}] in TSP during Non-Asian Dust and Asian Dust periods (units; ueq/m^3, ★; outlier).

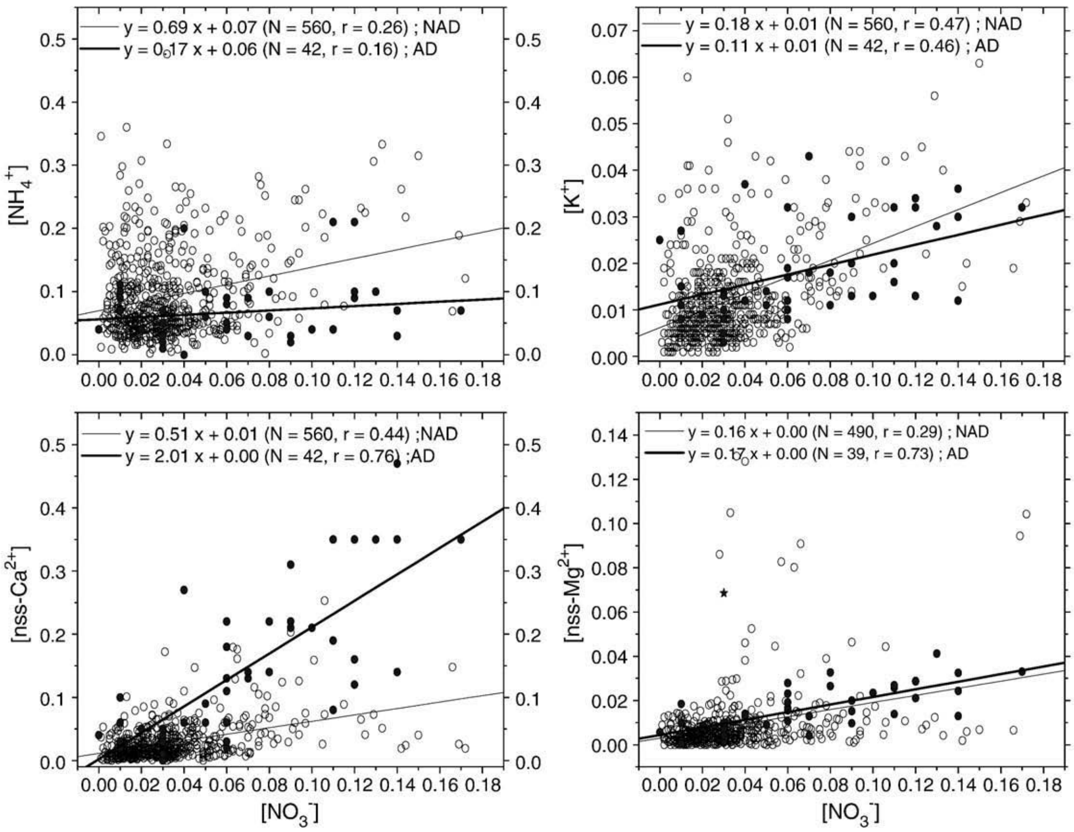

Fig. 10. Linear regression fits of [NH_4^+], [K^+], [nss-Ca^{2+}], and [nss-Mg^{2+}] against [NO_3^-] in TSP during Asian Dust and Non-Asian Dust periods (units; ueq/m^3, ★; outlier).

of TSP during AD periods. The slopes and correlation coefficients were very similar between nss-SO_4^{2-} and K^+ (slopes = 0.080 and 0.075; r = 0.75 and 0.73), indicating their strong associations during the spring season. The low slope values indicate the small portions of K^+ with nss-SO_4^{2-}. The slopes of the linear regression analyses between nss-Ca^{2+} and nss-SO_4^{2-} have shown high difference (slopes = 0.79 and 0.11) and the correlation coefficient was higher during AD period (r = 0.56) than that of NAD period (r = 0.37). On the other hand, the slope between nss-Mg^{2+} and nss-SO_4^{2-} was very low and they were weakly associated with each other even during AD periods (slope = 0.05; r = 0.42). These results imply that the interactions between gaseous acidic sulfur oxides and basic soil species in TSP may be strengthened during AD periods. But, nss-SO_4^{2-} was not associated with Na^+ during both periods (AD periods; r = 0.02, NAD periods; r = 0.10), unlikely in the case of the soil species.

The regression analyses between NO_3^- and NH_4^+, K^+, nss-Ca^{2+}, and nss-Mg^{2+} are shown in Fig. 10. The correlation coefficient between NO_3^- and nss-Ca^{2+} was high (r = 0.76) during AD periods, showing strong associations between them. Interestingly, the slope was larger than unity (slope = 2.10) during AD periods, demonstrating the possibility of nss-Ca^{2+} combining with other acidic anions such as CO_3^{2-} in TSP as explained in the previous section. Also NO_3^- was associated with nss-Mg^{2+} during AD periods (r = 0.73) although the contribution of nss-Mg^{2+} was expected to be small due to the low value of the slope (slope = 0.17) from the linear regression analyses. NO_3^- was similarly but weakly correlated with K^+ during both AD and NAD periods (r = 0.46 and 0.47). It is reasoned that K^+ is strongly associated with nss-SO_4^{2-} to form K_2SO_4 during both periods. It was interesting to note that NO_3^- was not correlated with NH_4^+ during AD or NAD periods (r = 0.16 and 0.26), although a previous study reported a moderate correlation (r = 0.68) between NH_4^+ and NO_3^- and a poor association between nss-Ca^{2+} and NO_3^- (r = 0.19) in fine mode particles at the Gosan site (Kim et al., 2004). Similarly, the NO_3^- was not associated with Na^+ during both periods (AD periods; r = 0.11, NAD periods; r = 0.29). In conclusion, the regression analyses suggested that NO_3^- could exist mainly as $Ca(NO_3)_2$ and partly as $Mg(NO_3)_2$ in the coarse mode in TSP during AD periods. Other studies have also demonstrated that NO_3^- was effectively produced from $Ca(NO_3)_2$ in the coarse mode in TSP (Zhuang et al., 1999; Evans et al., 2004; Pakkanen, 1996; Hwang and Ro, 2006). During NAD periods, it is assumed that NH_4NO_3 is partly formed from NO_3^- in the fine mode, since the correlations between NO_3^- and NH_4^+ were not strong due to the main associations of NH_4^+ and nss-SO_4^{2-}. Finally, we also calculated the concentration ratios of ionic species from arithmetic average values determined and they were summarized in Table 3. From the comparison of these results with the slopes of regression method (Figs. 9 and 10), they were

Table 3
The average concentrations and their ratios during Asian Dust (AD) and Non-Asian Dust (NAD) periods from February to May of 1992–2004.

	AD	NAD
Species (ueq/m³)		
nss-SO_4^{2-}	0.186	0.156
NO_3^-	0.071	0.033
NH_4^+	0.068	0.094
nss-Ca^{2+}	0.147	0.028
K^+	0.019	0.012
nss-Mg^{2+}	0.017	0.008
Concentration ratios		
NH_4^+/nss-SO_4^{2-}	0.37	0.60
K^+/nss-SO_4^{2-}	0.10	0.08
nss-Ca^{2+}/nss-SO_4^{2-}	0.79	0.18
nss-Mg^{2+}/nss-SO_4^{2-}	0.09	0.05
NH_4^+/NO_3^-	0.97	2.87
K^+/NO_3^-	0.26	0.38
nss-Ca^{2+}/NO_3^-	2.09	0.18
nss-Mg^{2+}/NO_3^-	0.24	0.26

comparable except NH_4^+/NO_3^-, which were not correlated with each other.

4. Conclusions

This study was for the measurement of total suspended particles at the Gosan site in Jeju Island, Korea from February to May of 1992–2004, in order to provide the valid information about AD effects on TSP compositions at a background area in Korea.

Among the water-soluble species, the concentrations of nss-SO_4^{2-} were the highest during AD and NAD periods, and those of nss-Ca^{2+}, increased highly during AD periods compared to those during NAD periods. Of the elemental species, the concentrations of S, Al, Fe, and Ca were as 10–100 times high as the levels of Zn, Cr, Pb, Ni, and Cu. The concentrations of the soil originated species, such as Al, Fe, and Ca, increased remarkably during AD periods. However, the concentrations of the anthropogenic species, such as S, Zn, Pb, Mo, and Cd, did not show much difference between AD and NAD periods, resulting that the soil-sourced species are much more contributive to AD particles compared to the anthropogenic species.

From the results of the ion balance between $[NH_4^+]_{eq}+[K^+]_{eq}+[\text{nss-}Ca^{2+}]_{eq}+[\text{nss-}Mg^{2+}]_{eq}$ and $[\text{nss-}SO_4^{2-}]_{eq}+[NO_3^-]_{eq}$, the slope was 1.09 during NAD periods, indicating a high neutralization tendency between the acidic anions and the basic cations. However, the slope was 0.77 during AD periods, showing the unbalance between the sums of cationic and anionic equivalent concentrations. In addition, CO_3^{2-} contributed up to 17% of the sum of anionic equivalent concentrations, playing an important role in the ion balance.

The elements such as Fe, Ca, Mg, Ti, Mn, Ba, Sr, V, and Co were all correlated with Al, which is a main soil particle component, and the slopes were similar during both AD and NAD periods. However, the elements S, Zn, Pb, Cu, Mo, and Cd did not show good correlations with Al, reasoning other possible sources, such as anthropogenic or industrial sources. Especially, the regression analysis results suggested a possibility of NO_3^- to be existed as $Ca(NO_3)_2$ and partly as $Mg(NO_3)_2$ in the coarse mode in TSP during AD periods.

Acknowledgements

This work was supported by the Korean Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2006-311-C00614). And this work was also supported in part by a research grant (PP09010) from the Korean Research Council of Public Science and Technology.

References

Arimoto, R., Duce, R.A., Savoie, D.L., Prospero, J.M., Talbot, R., Cullen, J.D., Tomza, U., Lewis, N.F., Ray, B.J., 1996. Relationship among aerosol constituents from Asia and the north Pacific during PEM-West A. J. Geophys. Res. 101, 2011–2023.
Arndt, R.L., Carmichael, G.R., Roorda, J.M., 1998. Seasonal source–receptor relationships in Asia. Atmos. Environ. 32 (8), 1397–1406.
Cao, J.J., Lee, S.C., Zhang, X.Y., Chow, J.C., An, Z.S., Ho, K.F., Watson, J.G., Fung, K., Wang, Y.Q., Shen, Z.X., 2005. Characterization of airborne carbonate over a site near Asian dust source regions during spring 2002 and its climate and environmental significance. J. Geophys. Res. 110, D03203.
Chen, L.-L., Carmichael, G.R., Hong, M.S., Ueda, H., Shim, S., Song, C.H., Kim, Y.P., Arimoto, R., Prospero, J., Savoie, D., Murano, K., Park, J.K., Lee, H.G., Kang, C., 1997. Influence of continental outflow events on the aerosol composition at Cheju Island, South Korea. J. Geophys. Res. 102, 28,551–28,574.
Chen, B., Hiroyuki, K.H., Dongmei, J., Hu, K., Lim, Jaesoo, 2008. Dust transport from northeastern China inferred from carbon isotopes of atmospheric dust carbonate. Atmos. Environ. 42, 4790–4796.
Chun, Y., Kim, J., Choi, J.C., Boo, K.O., Oh, S.N., Lee, M., 2001a. Characteristic number size distribution of aerosol during Asian dust period in Korea. Atmos. Environ. 35, 2715–2721.
Chun, Y., Boo, K.O., Kim, J., Park, S.U., Lee, M., 2001b. Synopsis, transport, and physical characteristics of Asian Dust in Korea. J. Geophys. Res. 106 (D16), 18,461–18,469.
Duce, R.A., Unni, C.K., Ray, B.J., Prospero, J.M., Merrill, J.T., 1980. Long-range atmospheric transport of soil dust from Asia to the Tropical North Pacific: temporal variability. Science 209, 1522–1524.
Evans, M.C., Campbell, S.W., Bhethanabotla, V., Poor, N.D., 2004. Effect of sea salt and calcium carbonate interactions with nitric acid on the direct dry deposition of nitrogen to Tampa Bay, Florida. Atmos. Environ. 38, 4847–4858.
Huebert, B.J., Bates, T., Russell, P.B., Shi, G., Kim, Y.J., Kawamura, K., Carmichael, G., Nakajima, T., 2003. An overview of ACE-Asia: strategies for quantifying the relationships between Asian aerosols and their climatic impacts. J. Geophys. Res. 108, 8633. doi: 10.1029/2003JD003550.
Hwang, H.J., Ro, C.U., 2006. Direct observation of nitrate and sulfate formations from mineral dust and sea-salts using low-Z particle electron probe X-ray microanalysis. Atmos. Environ. 40, 3869–3880.
Ishikawa, Y., Yoshimura, K., Mori, A., Hara, H., 1998. High sulfate and nitrate concentrations in precipitation at Nagasaki impacted by long-distant and local sources. Atmos. Environ. 32, 2939–2945.
Jaffe, D., Anderson, T., Covert, D., Kotchenruther, R., Trost, B., Danielson, J., Simpson, W., Berntsen, T., Karlsdottir, S., Blake, D., Harris, J., Camichael, G., Uno, I., 1999. Transport of Asia air pollution to North America. Geophys. Res. Lett. 26, 711–714.
Jaffe, D., McKendry, I., Anderson, T., Price, H., 2003. Six "new" episodes of trans-pacific transport of air pollutants. Atmos. Environ. 37, 391–404.
Kim, Y.P., Seinfeld, J.H., Saxena, P., 1993a. Atmospheric gas–aerosol equilibrium: I thermodynamic model. Aerosol Sci. Tech. 19, 157–181.
Kim, Y.P., Seinfeld, J.H., Saxena, P., 1993b. Atmospheric gas–aerosol equilibrium: II analysis of common approximations and activity coefficient calculation method. Aerosol Sci. Tech. 19, 182–198.
Kim, Y.P., Shim, S.G., Moon, K.C., 1998. Monitoring of air pollutants at Kosan, Cheju Island, Korea, during March–April 1994. J. Appl. Meteorol. 37, 1117–1126.
Kim, N.K., Kim, Y.P., Kang, C.H., Moon, K.C., 2004. Characteristics of nitrate concentration measured at Gosan: measurement data of PM2.5 and TSP between 1998 and 2002 (in Korean). J. Korean Soc. Atmos. Environ. 20, 119–128.
Lee, J.H., Kim, Y.P., Moon, K.C., Kim, H.K., Lee, J.B., 2001. Fine particles measurement at two background sites in Korea between 1996 and 1997. Atmos. Environ 35, 635–643.
Lee, Y.N., Weber, R.J., Ma, Y., Orsini, D., Maxwell, K., Blake, D., Meinardi, S., Sachse, G., Harward, C., Clarke, A.D., Moore, K., Kapustin, V.N., Chen, T.Y., Thorton, D.C., Tu, F.H., Bandy, A.R., 2003. Airborne measurement of inorganic ionic components of fine aerosol particles using the PILS-IC technique during ACE-ASIA and TRACE-P. J. Geophys. Res. 108 (D23), 8046.

Maxwell-Meier, K., Weber, R.J., Song, C.H., Orsini, D., Ma, Y., Carmichael, G.R., Streets, D., Blomquist, B., 2004. Inorganic composition of particles in mixed mineral dust-pollution plumes observed from ACE-ASIA. J. Geophys. Res. 109, D19507.

Park, J., Cho, S.Y., 1998. A long range transport of SO_2 and sulfate between Korea and East China. Atmos. Environ. 32, 2745–2756.

Park, M.H., Kim, Y.P., Kang, C.H., 2003. Aerosol composition change due to dust storm: measurements between 1992 and 1999 at Gosan, Korea. Water Air Soil Pollut. 3, 117–128.

Park, M.H., Kim, Y.P., Kang, C.H., Shim, S.G., 2004. Aerosol composition change between 1992 and 2002 at Gosan, Korea. J. Geophys. Res 109, D19S13.

Pakkanen, T., 1996. Study of formation of coarse particle nitrate aerosol. Atmos. Environ. 30, 2475–2482.

Perry, K.D., Cahill, A., Schnell, R.C., Harris, J.M., 1999. Long-range transport of anthropogenic aerosols to the National Oceanic and Atmospheric Administration baseline station at Mauna Loa Observatory, Hawaii. J. Geophy. Res. 104, 18,521–18,533.

Shimohara, T., Oishi, O., Utsunomiya, A., Mukai, H., Hatakeyama, S., Jang, E.S., Uno, I., Murano, K., 2001. Characterization of atmospheric air pollutants at two sites in northern Kyushu, Japan — chemical form, and chemical reaction. Atmos. Environ. 35, 667–681.

Song, C.H., Carmichael, G.R., 1999. The aging process of naturally emitted aerosol (sea-salt and mineral aerosol) during long range transport. Atmos. Environ. 33, 2203–2218.

Song, C.H., Carmichael, G.R., 2001. A three-dimensional modeling investigation of the evolution processes of dust and sea-salt particles in East Asia. J. Geophy. Res. 106, 18,131–18,154.

Song, C.H., Maxwell-Meier, K., Weber, R.J., Kapustin, V., Clarke, A., 2005. Dust composition and mixing state inferred from airborne composition measurements during ACE-Asia C 130 Flight #6. Atmos. Environ. 39, 2203–2218.

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.-H., Yarber, K.F., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. J. Geophy. Res. 108 (D21), GTE 30–1. doi: 10.1029/2002JD003093.

Sullivan, R.C., Guazzotti, S.A., Sodeman, D.A., Prather, K.A., 2007. Direct observations of atmospheric processing of Asian mineral dust. Atmos. Chem. Phys. 7, 1213–1236.

Talbot, R.W., Dibb, J.E., Leffer, B.L., Bradshaw, J.D., Sandholm, S.T., Blake, D.R., Blake, N.J., Sachse, G.W., Collins, J.E., Heikes, B.G., Merrill, J.T., Gregory, G.L., Anderson, B.E., Singh, H.B., Thornton, D.C., Bandy, A.R., Pueschel, R.F., 1997. Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during February–March 1994: results from PEM-West B. J. Geophys. Res. 102, 28,255–28,274.

Taylor, McLennan, 1985. The Continental Crust: Its Composition and Evolution. Blackwell Sci., Cambridge, Mass., p. 46.

Zhang, D., Iwasaka, Y., 2001. Chorine deposition on dust particles in marine atmosphere. Geophys. Res. Lett. 28, 3613–3616.

Zhuang, H., Chan, C.K., Fang, M., Wexler, A.S., 1999. Formation of nitrate and non-sea-salt sulfate on coarse particles. Atmos. Environ. 33, 4223–4233.