

## Seasonal Size Distribution of Atmospheric Particles in Iksan, Korea

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**Abstract:** During a twenty-day period in 2005, a nine-stage Andersen cascade impactor was used to determine the seasonal size distribution of atmospheric particles and its inorganic ion species sampled for 24hr in Iksan city, located southwest of the Korean peninsula. Samples were analyzed for major water-soluble ion species using Dionex-100 ion chromatograph. Average fine and coarse mass concentrations of atmospheric particles were, respectively, 31.4 and 82.6  $\mu\text{g m}^{-3}$  in spring and 35.8 and 73.4  $\mu\text{g m}^{-3}$  in fall-winter during the sampling period of 2005, while measurements of 69.8 and 9.9 were obtained in the sampling period of summer. The size distribution of particulate mass concentration during the non-Asian dust period was generally bimodal, whereas the size distribution of particulate mass concentration during the Asian dust period was unimodal due to the significant increase of coarse particles, which originated from long-range transport of soil dust particles from loess regions of the Asian continent. Among ionic species,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{K}^+$  were mainly distributed in fine particles due to their characteristics of emission sources and gas-to-particle conversion, while  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were dominantly in coarse particles. However,  $\text{NO}_3^-$  and  $\text{Cl}^-$  were distributed in both coarse particles and fine particles. Although  $\text{SO}_4^{2-}$  was mainly distributed in fine particles, the size distributions of  $\text{SO}_4^{2-}$  in coarse mode were significantly increased during the Asian dust events compared to those during the non-Asian dust period.  $\text{Ca}^{2+}$  showed the most abundant species in the atmospheric particles during the Asian dust period.  $\text{NH}_4^+$  was found to mainly exist as  $(\text{NH}_4)_2\text{SO}_4$  in fine particles.

**Keywords:** andersen cascade impactor, size distribution, water-soluble ion species, fine and coarse particles, Asian dust

### Introduction

In the east Asian region, including Korea, huge amount of  $\text{SO}_2$ ,  $\text{NO}_x$ , and anthropogenic species as well as mineral dust are observed. Especially, the Korean peninsular, which extends southward from northeast part of the Asian continent, is expected to be influenced by anthropogenic air pollutants and soil dust, transported by prevailing winds across the Yellow Sea from the Asian continent. Soil dust particles originating from the loess regions of the Asian continent, called Asian dust, are transported to Korea, Japan, as well as northern Pacific Ocean (Kang *et al.*, 2005; Han *et al.*, 2004; Mori *et al.*, 2003). These particles result in a number of environmental influences including visibility impairment and heavy metal deposition (Kim *et al.*, 2001; Shin *et al.*, 1996). They also

affect the atmospheric gas-aerosol chemical equilibrium by interacting with the acidic gaseous pollutants due to their alkaline characteristics (Vogt *et al.*, 2005; Park *et al.*, 2004). Atmospheric particles are divided into two categories: the primary particles generated from both anthropogenic and natural sources, and the secondary particles produced by gas-to-particle conversion processes in the atmosphere. Particles emitted from different sources usually have different particle size distribution and chemical composition. Fine particles are generally emitted from anthropogenic sources such as motor vehicles and various facilities with combustion processes of fossil fuel or are produced by gas-to-particle conversion, while coarse particles are mainly generated from natural sources like sea salt and soil dust. Therefore, measurements on the particle size distribution and chemical composition of atmospheric particles would be important for understanding their physical and chemical characteristics, sources, and formation mechanism (Park *et al.*, 2004; Ynoue and Andrade, 2004; Pagano *et al.*,

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1998).

Several field studies for the particle size distribution have been performed mainly in urban areas of Korea. However, most of these studies have focused on measurements collected for several days or one week (Park *et al.*, 2004; Kim and Kim, 2000; Shin *et al.*, 1996). Measurements for mass size distribution of water-soluble ionic species for one day are seldom carried out.

The purpose of this study is to investigate the size distribution of mass concentrations as well as its water-soluble inorganic ions of the 24-hr integrated atmospheric particles using a nine-stage Andersen cascade impactor in Iksan city, located southwest of the Korean peninsula for each season, 2005. In order to interpret the size distribution of atmospheric particles, particles with an aerodynamic diameter less than 2.1  $\mu\text{m}$  were classified in fine particulate matter (FPM) and particles with an aerodynamic diameter more than 2.1  $\mu\text{m}$  were classified in coarse particulate matter (CPM), respectively. The effects of Asian dust on the airborne particles in conjunction with their episodes with higher particulate concentrations were also examined in terms of the size distribution of water-soluble inorganic ion

species. Particulate matter with 10  $\mu\text{m}$  and 2.5  $\mu\text{m}$  aerodynamic diameters ( $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , respectively) were also measured, but the detailed results will be reported elsewhere.

## Methods

Twenty-four hr integrated measurements of size distribution of atmospheric particles were carried out at Iksan (35.9661° latitude, 126.9556° longitude), Korea. Table 1 stands for sampling description and total concentrations obtained the summing of all impactor stages and the backup filter measured by an Andersen cascade impactor. These sampling periods were considered to be representative of each season, although those were not obtained enough. Atmospheric particles samples were collected on the rooftop of Iksan Chamber of Commerce and Industry building (about 20 m above ground level). The sampling site is located in the downtown of Iksan, which is a small city located 200 km south of Seoul, the metropolitan urban city of South Korea (Fig. 1). The sampling site is also approximately 50 km west from the coastline of the Yellow Sea and surrounded by residential and commercial zones.

**Table 1.** Sampling description and total concentrations obtained by the summing of all impactor stages and the backup filter measured by an Andersen cascade impactor

Season	Sampling day	Sampling time	Duration time (hours)	Total concentration ( $\mu\text{g m}^{-3}$ )
Spring	4/20 day*	7:31 a.m.-7:16 p.m.	11.7	220.6
	4/20 night	8:31 p.m.-6:47 a.m.	10.3	110.7
	4/21	7:19 a.m.-6:40 a.m.	23.4	87.7
	4/22	7:10 a.m.-7:13 a.m.	24.0	100.3
	4/23	7:41 a.m.-8:03 a.m.	24.4	50.4
Summer	7/25	7:45 a.m.-7:32 a.m.	23.8	127.6
	8/4-8/5	10:30 a.m.-7:19 a.m.	44.8	31.9
Fall & Winter	11/6 night*	6:50 p.m.-7:30 a.m.	12.7	517.4
	11/7*	8:00 a.m.-7:25 a.m.	23.4	135.2
	11/8	7:55 a.m.-7:32 a.m.	23.6	45.5
	11/9	7:58 a.m.-6:50 a.m.	22.9	57.0
	11/28	8:05 a.m.-7:35 a.m.	23.5	71.2
	11/29-11/30	8:04 a.m.-7:43 a.m.	47.7	57.5
	12/1	8:05 a.m.-7:50 a.m.	23.8	95.9
	12/2-12/3	8:10 a.m.-9:02 a.m.	48.9	24.6
	12/6	8:10 a.m.-7:52 a.m.	23.7	61.4
	12/7-8D	8:26 a.m.-5:30 p.m.	33.1	26.1

\*In this sampling day, Korea Meteorological Administration (KMA) has reported the occurrence of Asian dust storms.

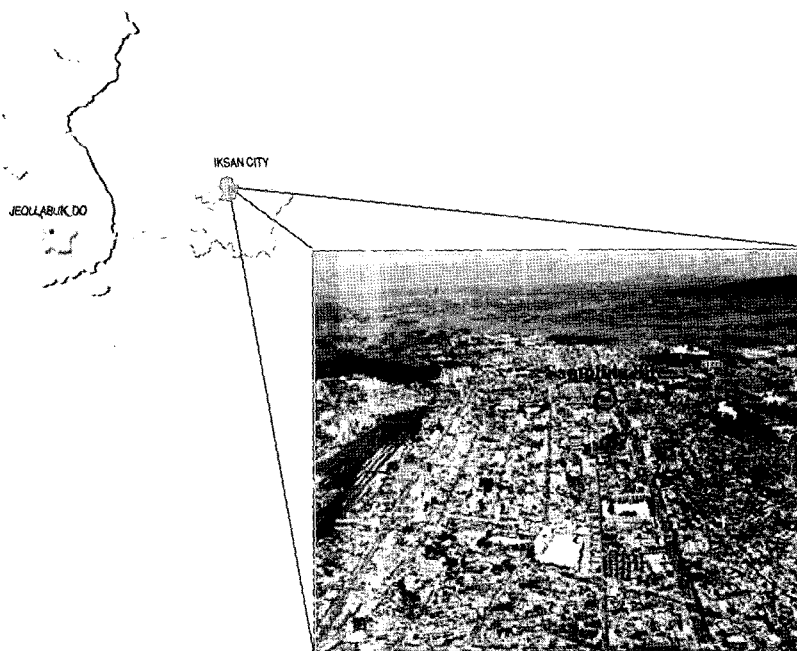


Fig. 1. Location of Iksan city in Korean peninsula and the sampling site.

Iksan city hall is about 100 m north from the sampling site. The Iksan industrial complex is located several kilometers east from the sampling site. The population of Iksan is about 0.33 million people in a 507.11 km<sup>2</sup> area with 98 thousand motor vehicles registered. Iksan city is also surrounded by agricultural zone outside a 5 km radius from the sampling site of Iksan Chamber of Commerce and Industry building. These suggest that the air quality of Iksan has been affected by urban and industrial emissions, the burning of agriculture waste, and long-range transported pollutants. For more details on the local conditions of the sampling site and atmospheric particle collection methodologies refer to Kang and Lee (2005b).

The size distribution of atmospheric particles was measured with an Andersen cascade impactor (Model KA-200, Koritsu Instruments Co., Japan), which employs nine filters to separate particles with aerodynamic cutoff diameters ( $d_{50}$ ) of < 0.43, 0.43~0.65, 0.65~1.1, 1.1~2.1, 2.1~3.3, 3.3~4.7, 4.7~7.0, 7.0~11, and >11  $\mu\text{m}$ . Particles were collected onto 81 mm polyethylene sheet filters placed on eight collection plates from the top stage of the sampler, and a 0.45  $\mu\text{m}$  pore-size quartz fiber filter

with a diameter of 81 mm was used at the lowest stage of the sampler to collect those particles that had a  $d_{50}$  of less than 0.43  $\mu\text{m}$ . The sampler operated at a flow rate of 28.3 l/min with an integration time of 24 hr from early morning to early morning of next day (Table 1). During the Asian dust storm period, however, the sampling interval was divided into two times a day, daytime (from 7 a.m. to 7 p.m.) and nighttime (from 7 p.m. to 7 a.m.), respectively. The Asian dust storms were observed two times in this period, on April 20 and November 6-7, according to the official announcement of Korea Meteorological Administration (KMA). Except for these days 2005, KMA presented additionally 3 times occurrence of the Asian dust storms on March 29, April 7-8, and April 10-11, respectively (METRI AMRL Homepage). During the study period, 17 sets of samples for mass size distribution were taken.

Filter preparation, handling, and extraction were made according to the procedures recommended by the United States Environmental Protection Agency (US EPA, 1999). Mass concentrations of atmospheric particles in terms of the size distribution were obtained gravimetrically using an electronic

balance with a sensitivity of 1 µg. Filters were equilibrated for 24 hr prior to weighing. Filters were also stored in a desiccator before sampling to eliminate the effect of humidity and in a 4°C refrigerator prior to chemical analysis after sampling. Sampled aerosols on polyethylene sheets were extracted with 10 ml deionized water in an ultrasonic bath for 20 min, while quartz fiber filter was extracted with 20 ml deionized water in the same condition. All the extraction solutions were filtered by using syringe filter with 0.45 µm pore-size (Millex®HV 13 mm, Millipore) and stored in plastic vials at 4°C until analyzed. The aqueous extract was analyzed for water-soluble inorganic ion species (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) using DX-100 ion chromatography (Dionex Inc., USA), equipped with a CDM-3 electric conductivity detector. Calibration curves were constructed from the peak areas of the chromatographs produced from a series of mixed standards (IC-MCA-02-1 for cation analysis, IC-MAN-18-1 for anion analysis, AccuStandard Inc., USA). Filter blanks were also prepared in the same manner as above mentioned and analyzed for the water-soluble ionic species. The concentrations of ions were calculated by considering the analytical results of blank filters.

The analytical uncertainties were checked by calculating relative standard deviation (RSD) obtained from replicate sample injections, as shown in Equation (1). To obtain a pooled estimate of the standard deviation,  $S_{pooled}$  deviations from the mean for each subset are squared; the squares of all subsets are then summed and divided by an appropriate number of degree of freedom, as shown in Equation (2). The pooled  $s$  is obtained by extracting the square root of the quotient. One degree of freedom is lost for each subset. Thus, the number of degrees of freedom for the pooled  $s$  is equal to the total number of measurements minus the number of subsets. Where  $N_1$  is the number of data in set 1,

$N_2$  is the number in set 2, and so forth. The term  $N_s$  is the number of data sets that are being pooled.

$$RSD(\%) = \frac{S_{pooled}}{\bar{x}_{all}} \times 100 \quad (1)$$

$$S_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1} (x_i - \bar{x}_1)^2 + \sum_{j=1}^{N_2} (x_j - \bar{x}_2)^2 + \sum_{k=1}^{N_3} (x_k - \bar{x}_3)^2 + \dots}{N_1 + N_2 + N_3 + \dots - N_s}} \quad (2)$$

Table 2 shows the mean concentration of replicate samples and RSD for cations and anions measured from polyethylene sheets with a diameter of 81 mm from stage 0 to stage 7 as well as for cations and anions measured from backup filter of quartz fiber with a diameter of 81 mm at the lowest stage of Andersen cascade sampler. The RSDs for all cations and anions of polyethylene sheets (stage 0-7) were found to be less than 8% and 6%, respectively. The RSDs for backup filters were less than 2% in both cations and anions, which were lower than those for polyethylene sheet due to higher concentration of all ions in the backup filters. In addition, the average RSD for both pre- and post-weights of filters was less than 0.002%, indicating reliability of the weighing process and corresponding outcome.

Meteorological observation was made at the Jeollabuk-Do Agricultural Research & Extension Services that designed to record the data of AWS (Automatic Weather Station) and located 3.3 km east from the sampling site. For a correct interpretation of analytical result of atmospheric particle, precipitation data is very important. Therefore, the data of precipitation amount were collected by the AWS and arranged in accordance with the sampling period.

## Results and Discussion

### Meteorological Conditions

Fig. 2 shows the wind rose of hourly AWS data

**Table 2.** Uncertainties of water-soluble inorganic ion species for IC analysis of replicate samples

		Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Stage 0-7	Conc. (ppm)	0.68	0.24	0.09	0.15	0.96	0.91	2.48	2.19
	RSD (%)	4.71	7.14	8.06	3.10	2.14	5.68	2.77	4.15
Backup	Conc. (ppm)	4.78	4.83	0.24	0.22	2.31	1.41	3.31	7.91
	RSD (%)	0.86	1.64	0.30	0.33	0.67	2.41	2.08	1.98

for all months 2005 as well as each season of spring (March-May), summer (June-August), and fall-winter (November-December). During the sampling period of fall-winter, there are partially some meteorological data omitted at the end of November and the beginning of December, respectively. From

the seasonal profile of wind rose, it was known that there were seasonal differences in prevailing wind direction. During spring the prevailing wind are from the west, during summer the warm winds are dominantly between the west and south, and during fall-winter the prevailing cold winds are

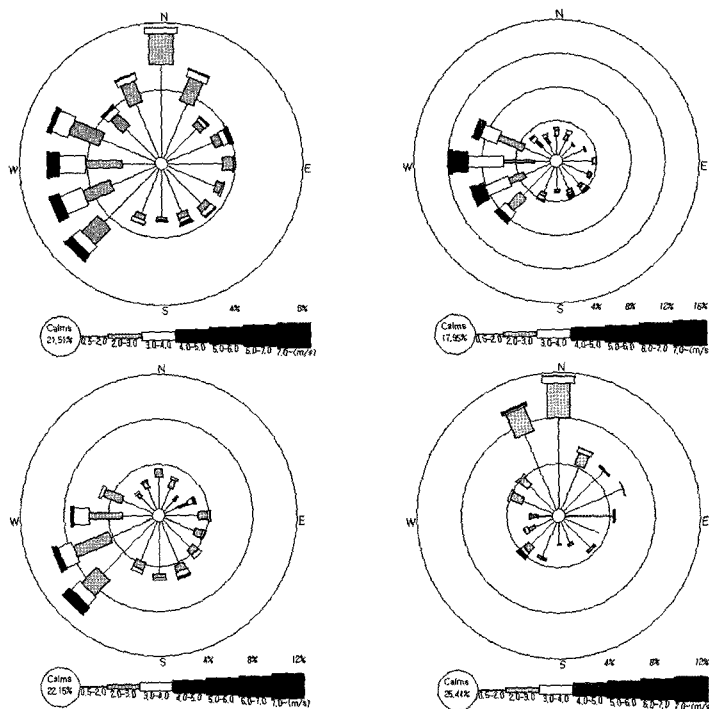


Fig. 2. Wind rose for all months 2005 (above left), March-May (above right), June-August (below left), and November-December (below right) in Iksan.

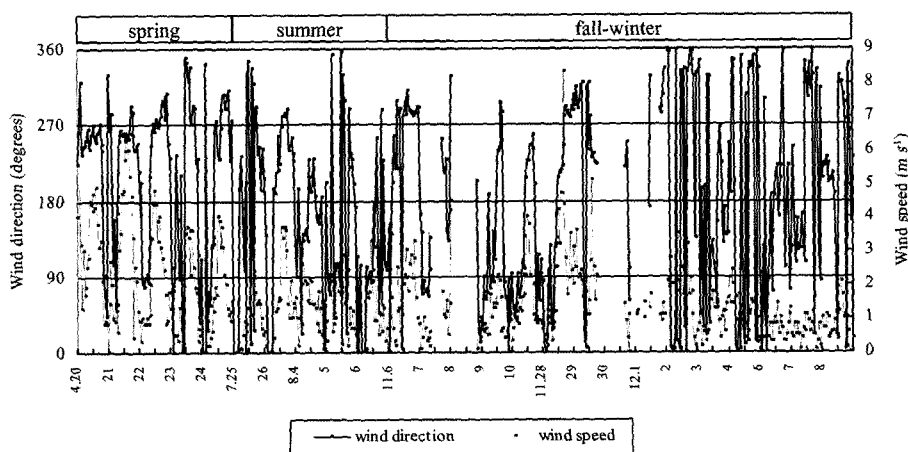


Fig. 3. Temporal variation of wind direction (degrees) and wind speed ( $m s^{-1}$ ) during the sampling period in Iksan.

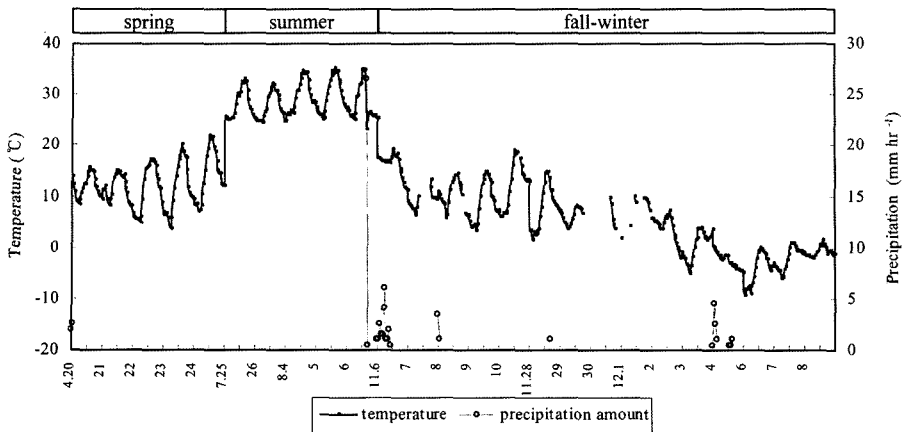


Fig. 4. Temporal variation of temperature (°C) and precipitation amount (mm hr<sup>-1</sup>) during the sampling period in Iksan.

from the north, respectively. Temporal variation of wind directions and wind speed during the sampling period is presented in Fig. 3. Although temporal variation of wind direction was fluctuational, its general pattern reflected seasonal trend as showed in Fig. 2. Fig. 4 shows temporal variation of temperature and precipitation amount observed by the hour in Iksan. Hourly average atmospheric temperature and wind speed during the sampling days are 11.4°C and 2.2 m/sec for spring, 29.2°C

and 1.06 m/sec for summer, and 4.4°C and 1.4 m/sec for fall-winter, respectively. The general meteorological weather conditions in Iksan are characterized by a cool and dry fall-winter from November to December and a hot and humid summer from July to August. In relation to the precipitation event before and during the sampling day, precipitation phenomenon was observed before April 20D, August 4-5, and November 6N, as well as during November 7 and 28, December 2-3. In addition,

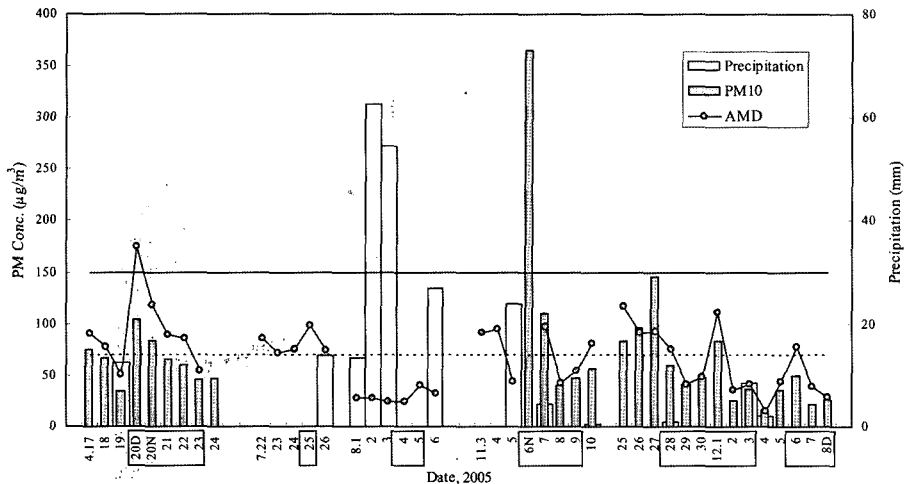


Fig. 5. Temporal variation of PM<sub>10</sub> mass concentration and precipitation. The solid horizontal line indicates 24 hr Korean National Ambient Air Quality Standard (NAAQS) for PM<sub>10</sub> of 150 µg m<sup>-3</sup> and the dashed horizontal line means annual NAAQS for PM<sub>10</sub> of 70 µg m<sup>-3</sup>, respectively. Symbols of D and N on the x-axis indicate daytime and nighttime, respectively. AMD indicates data obtained from the air quality automatic network monitoring of Korean government agency (Ministry of Environment). Dates in the rectangular boxes are days of measuring mass size distribution of atmospheric aerosols.

heavy snow has fallen on December 3-4 before the sampling days of December 6~8D. The snow depth was more than approximate 20 cm from the surface.

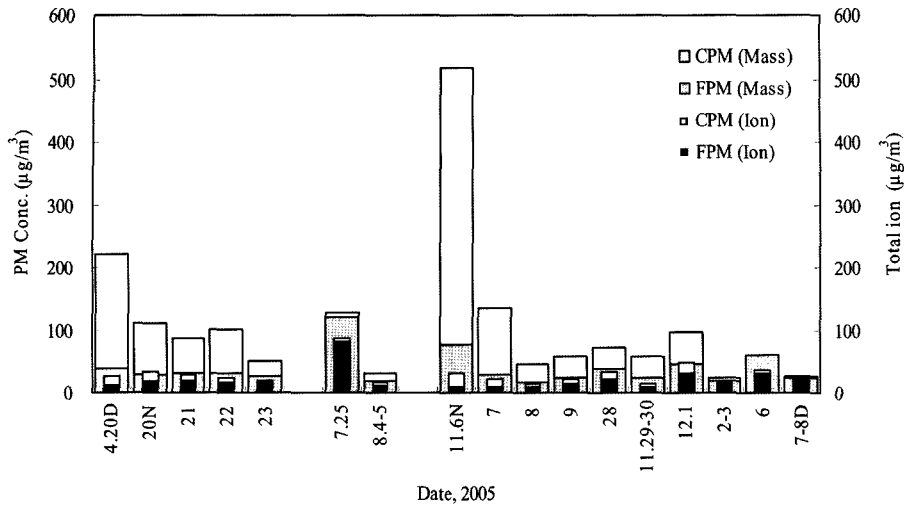
### Mass Concentration of Atmospheric PM<sub>10</sub>

Fig. 5 shows the mass concentrations of PM<sub>10</sub> and precipitation amount in relation to the measurement period of mass size distribution of Iksan atmospheric particles. In this figure, the mass concentrations data of PM<sub>10</sub> were obtained from both our field project and a Ministry of Environment air monitoring station in Iksan in 2005, respectively. The solid horizontal line indicates the 24 hr ambient air quality standard for PM<sub>10</sub> of 150  $\mu\text{g m}^{-3}$  and the dashed horizontal line means the annual ambient air quality standard for PM<sub>10</sub> of 70  $\mu\text{g m}^{-3}$ , respectively. Symbols of D and N on the x-axis indicate daytime and nighttime, respectively. However, there are no data of PM<sub>10</sub> concentration available in some cases. Our field measurement of PM<sub>10</sub> concentration failed in July and August because the airflow controller installed in the pump was out of order during this sampling period. One sample of 6N for government data is also missing due to sampling error. The dates in the rectangle on the x-axis of the figure mean the sampling days of mass size distribution for Iksan atmospheric particles. To consider the effect of meteorological condition such as a precipitation on the mass concentration of particles, the concentrations of PM<sub>10</sub> in this figure were plotted from 3 days before the first measurement of mass size distribution. The high concentrations of PM<sub>10</sub> were observed during the Asian dust storm events of April 20 and November 6, as well as in the non-Asian dust event of November 27. Extremely high level of PM<sub>10</sub> was observed during the night of November 6, when a strong Asian dust storm passed over Iksan. This is an unusual event because most of Asian dust storms usually occur during spring in Korea and Japan. Although precipitation more than 10 mm rainfall amount on the days (April 19 and November 5~6D) before two events of the Asian dust storm were observed, the mass concentration of particles showed episodic cases compared to other samples. The measurement data of the size distribution for mass concentration and its ion species for these particle samples could be very helpful in understanding the essential

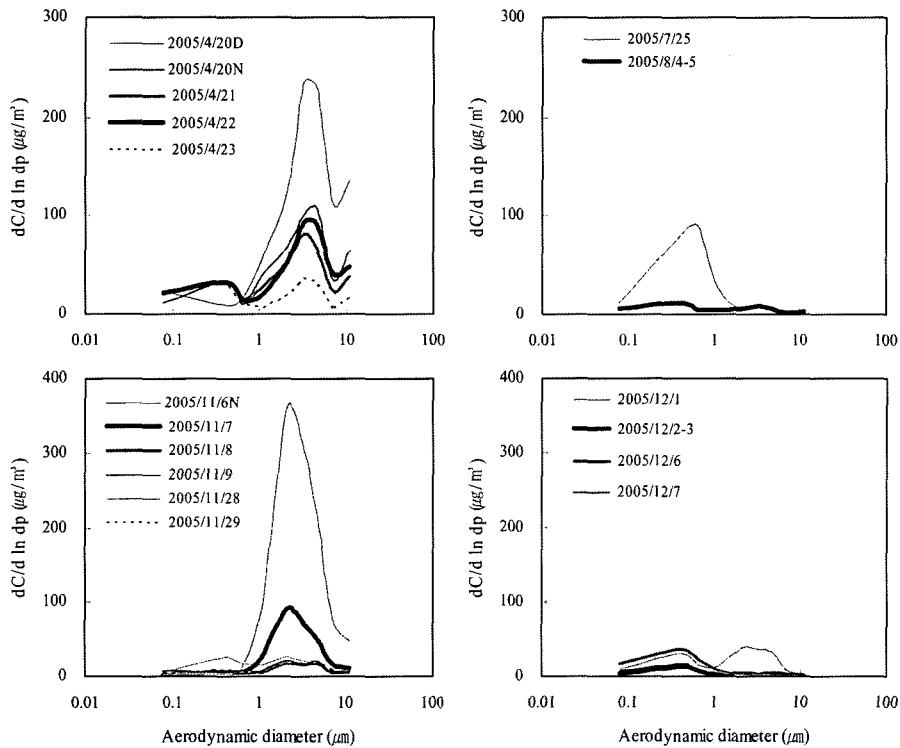
chemical characteristics of Asian dust long-range transported from the Asian continent since precipitation amount seems to be enough to scavenge local air pollutants in the atmosphere. In summer, there has been continually much rain for a few days before August 4-5. Accordingly, the concentrations of components of particle sample collected on August 4-5 are expected to be lower compared those on July 25 in spite of the same seasonal characteristics of summer.

### Mass Concentration of Fine and Coarse Particulate Matter

The total mass concentration of atmospheric particles, obtained by the summing of all stages, can be seen in Table 1. The highest concentration was 517.4  $\mu\text{g m}^{-3}$ , which measured on November 6N, whereas the lowest concentration was 26.1  $\mu\text{g m}^{-3}$ , which measured on December 7-8D. Fine particulate matter (FPM) concentrations were obtained by the summing of stages (stage 5~7 and backup) having a  $d_{50}$  of less than 2.1  $\mu\text{m}$ , and coarse particulate matter (CPM) concentrations were obtained by the summing of stages (stage 0~4) having a  $d_{50}$  of more than 2.1  $\mu\text{m}$ . Temporal variations of the mass concentration and total ion concentration are shown in Fig. 6. Average fine and coarse mass concentrations of atmospheric particles were, respectively, 31.4 and 82.6  $\mu\text{g m}^{-3}$  in spring and 35.8 and 73.4  $\mu\text{g m}^{-3}$  in fall-winter during the sampling period of 2005, while measurements of 69.8 and 9.9 were obtained in the sampling period of summer. Exceptionally high FPM concentration was observed on July 25, which impacted heavily on local air quality. The FPM increase in that day was probably caused by a higher photochemical reaction rate (higher maximum temperature) in the atmosphere under stagnant meteorological conditions. In spring, the mass concentration of CPM showed generally higher than that of FPM, especially 4.6 times higher on April 20D, when Asian dust storm was observed in both Iksan and Korean peninsula, in addition to rain falling before the day. During the night of November 6, when strong Asian dust storm was also observed, the mass concentration of CPM showed 5.6 times higher than that of FPM. During the sampling period of after this Asian dust storm the contribution of



**Fig. 6.** Temporal variation of FPM and CPM calculated by the summing of the mass concentration (broad bar) and total ion concentration (narrow bar) in stages with a  $d_{50}$  of less than  $2.1 \mu\text{m}$  (considered FPM) and in those with a  $d_{50}$  of more than  $2.1 \mu\text{m}$  (considered CPM) for the atmospheric particles during the sampling period.

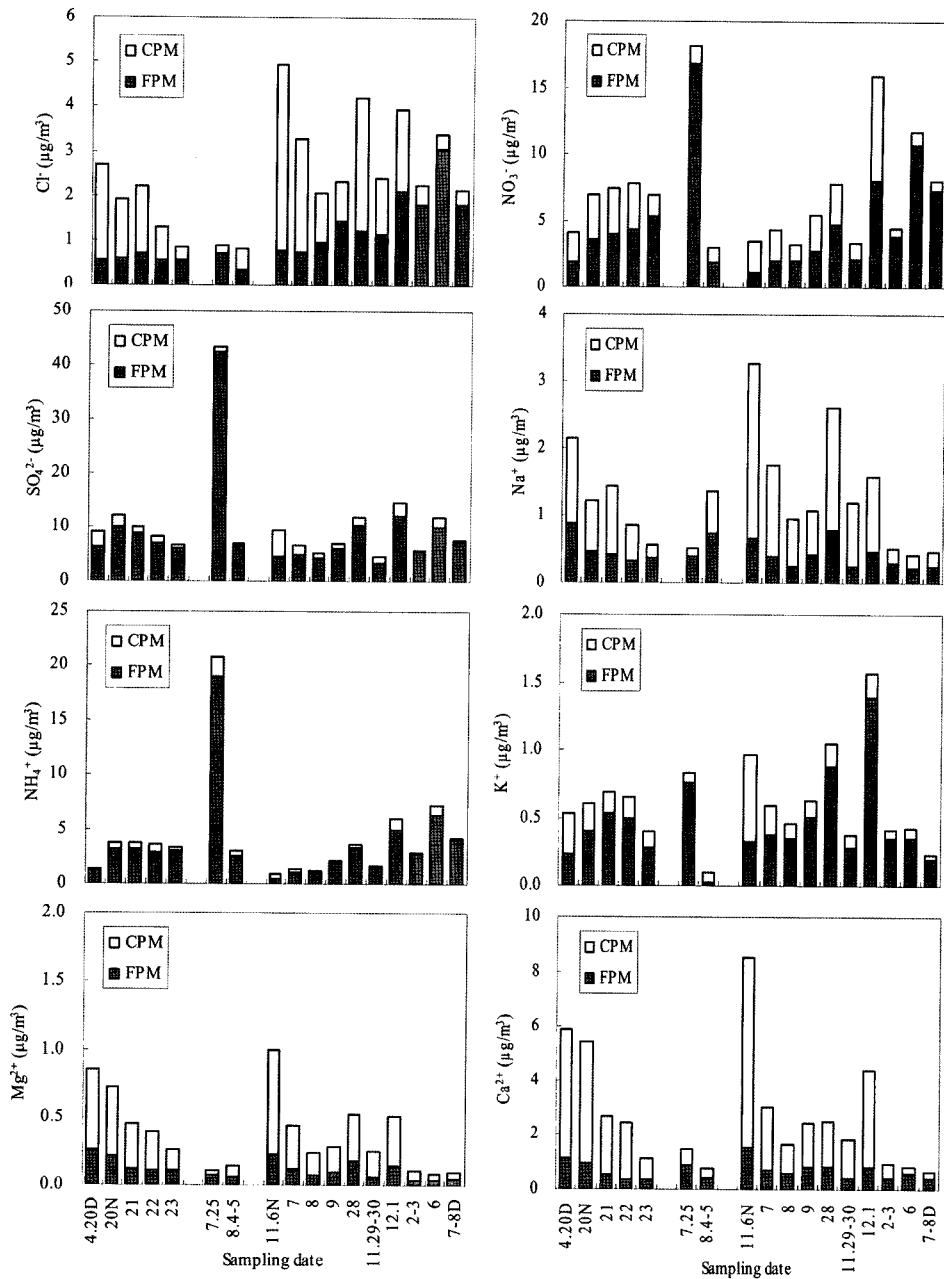


**Fig. 7.** Seasonal size distribution of mass concentration in the atmospheric particles.

CPM were generally decreased, whereas they were dramatically dropped after snow has fallen on

December 3-4. This trend maintained until the sampling days of December 6~8D. The reason of





**Fig. 8.** Temporal variation of FPM and CPM calculated by the summing of ion concentration in stages with a  $d_{50}$  of less than  $2.1 \mu\text{m}$  (considered FPM) and in those with a  $d_{50}$  of more than  $2.1 \mu\text{m}$  (considered CPM) for the atmospheric particles during the sampling period.

this rapid decrease in CPM mass concentration is still unclear at this point.

Fig. 7 shows the mass size distribution of the atmospheric particles collected Iksan during this

study. The mass size distribution of atmospheric particles is generally known to be bimodal, with one peak in the fine mode and the other in the coarse mode. During the Asian dust period, however,

the mass concentration of atmospheric particles showed a unimodal distribution with a predominant peak in the 3.3–4.7  $\mu\text{m}$  range for April 20 daytime and in the 2.1–3.3  $\mu\text{m}$  range for November 6 nighttime. The results suggest that the significant increase of coarse particles during the Asian dust period caused transition of particle size distribution from bimodal to unimodal. Fig. 8 shows the temporal variation of FPM and CPM calculated by the summing of ion concentration in stages with a  $d_{50}$  of less than 2.1  $\mu\text{m}$  and in those with a  $d_{50}$  of more than 2.1  $\mu\text{m}$  for the atmospheric particles during the sampling period of 2005 in Iksan. Among ion species, it was found that  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  were mainly distributed in fine particles, while  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were dominantly in coarse particles. Fine particle mode species may be emitted from combustion of fossil fuels or transformed through atmospheric chemical reactions between gaseous precursors and free radicals and sunlight. Sulfate, nitrate, and ammonium are known to be representative compounds of secondary

formation of particles in the air and converted by atmospheric reactions from  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ , respectively (Kang and Lee, 2005a; Vogt *et al.*, 2005; Ma *et al.*, 2005; Park *et al.*, 2004). However,  $\text{NO}_3^-$  and  $\text{Cl}^-$  were distributed in both coarse particles and fine particles. It indicates that  $\text{NO}_3^-$  and  $\text{Cl}^-$  can exist in either fine or coarse particle mode, based on the reactions of formation with other compounds.  $\text{NO}_3^-$  can be distributed in fine mode when it is formed from nitrogen oxides, precursors of particulate  $\text{NO}_3^-$ , through reactions with  $\text{NH}_3$  (Cheng *et al.*, 2000). Also, reaction with sea salts is a major route to form coarse-mode  $\text{NO}_3^-$  particles (Wakamatsu *et al.*, 1996; Cheng *et al.*, 2000). Thus, coarse mode  $\text{NO}_3^-$  in this study was ascribed to the reaction of gas phase nitric acid with sea salt during the non-Asian dust period, but with soil particles during the Asian dust period.  $\text{NO}_3^-$  formation during the non-Asian dust period by reaction of nitric acid and sea salt particles, however, could not be proved by a quantitative analysis due to the filter sampling artifacts and the

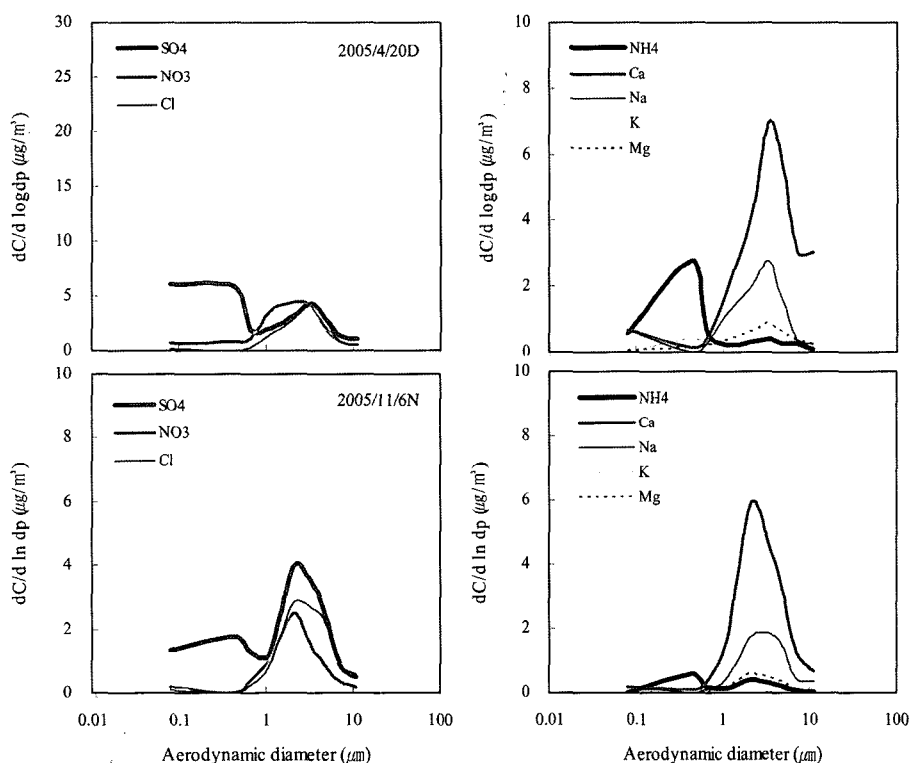


Fig. 9. Size distribution of chemical species in the atmospheric particles for the Asian dust period.

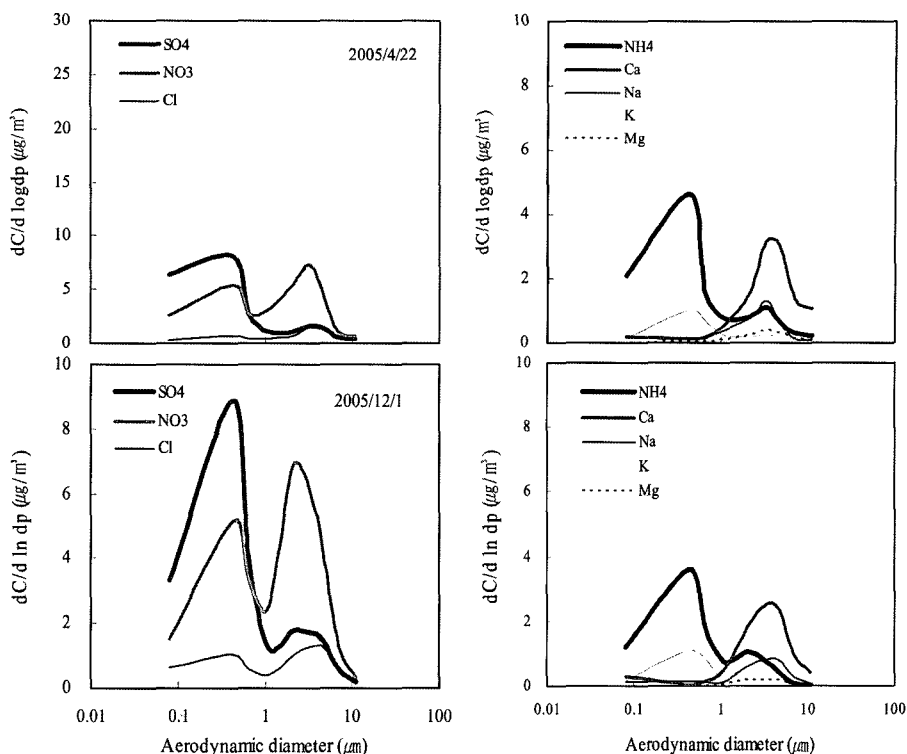


Fig. 10. Size distribution of chemical species in the atmospheric particles for the non-Asian dust period.

lack of gas phase species measurements. It is believed that coarse  $\text{Cl}^-$  and  $\text{Na}^+$  originated from sea-salt particles and that Asian dust storms arriving at Iksan contain considerable amount of sea-salt particles due to their passage over the Yellow Sea from the China continent.  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  may originate from soil dust particles.  $\text{Ca}^{2+}$  showed the greatest increase during the Asian dust period, compared to the non-Asian dust period.

Fig. 9 indicates the size distribution of water-soluble ionic species in the atmospheric particles for the Asian dust storms. Fig. 10 shows the size distribution of same chemical species for the representative cases of the non-Asian dust periods. During the Asian dust period, the dominant ionic species were found to be  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in anion and cation with a peak in the 3.3–4.7  $\mu\text{m}$  range for April 20 daytime and in the 2.1–3.3  $\mu\text{m}$  range for November 6 nighttime, respectively. The size distributions of  $\text{SO}_4^{2-}$  show a bimodal mode with one peak in the fine mode and the other in the coarse mode, while  $\text{Ca}^{2+}$  indicate an unimodal

distribution, showing big increase of coarse particles for the Asian dust storm events compared to the non-Asian dust period. One important point that should be noted from Fig. 9 and 10 is the significant increase of coarse  $\text{SO}_4^{2-}$  compared to that in the non-Asian dust period. Coarse  $\text{SO}_4^{2-}$  may be produced by heterogeneous oxidation of sulfur dioxide gas on the wet surface of alkaline soil particles. It was also reported that most sulfur components existed as  $\text{CaSO}_4$  in soil dust particles (Kang *et al.*, 2005a; Park *et al.*, 2004). Considering a predominant peak of  $\text{Ca}^{2+}$  in coarse mode, it is believed that that large fraction of coarse sulfate may be from the reaction of heterogeneous  $\text{SO}_2$  and soil dusts as well as existed in the neutralized chemical component of  $\text{CaSO}_4$ .

During the non-Asian dust,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were dominant in anion and showed bimodal distribution:  $\text{SO}_4^{2-}$  was more dominant in fine mode than in coarse mode, while nitrate showed higher peak in the coarse mode than in the fine mode. Among the cations, ammonium and calcium were dominant.

Ammonium mainly existed in fine mode, while calcium was in coarse mode. Fine particulate ammonium may originate from the reaction of  $\text{NH}_3$  with some acidic forming particles in the fine mode. Alternatively, the  $\text{NH}_3$  vapor may condense on an acidic particle surface of anthropogenic origin and accumulate in the fine mode.  $\text{NH}_3$  reacts with acidic gases such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  in the atmosphere. The stability of the reaction products is different:  $(\text{NH}_4)_2\text{SO}_4$  is the most stable, while  $\text{NH}_4\text{Cl}$  is the most volatile. Therefore,  $\text{NH}_3$  prefers to react with  $\text{H}_2\text{SO}_4$  or  $\text{SO}_4^{2-}$ . Considering this fact and the size distribution of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  measured in the atmospheric particles during the non-Asian dust period,  $\text{NH}_4^+$  in fine particles may mainly exist in the neutralized chemical components of  $(\text{NH}_4)_2\text{SO}_4$ . From Fig. 8 and 10,  $\text{K}^+$  was also dominantly distributed in fine particles. According to the study of post-harvest biomass burning aerosols in Gwangju, Korea,  $\text{K}^+$  is known to be a highly useful tracer for pyrogenic aerosols because the combustion of plant matter, which contains  $\text{K}^+$  as a major electrolyte within its cytoplasm, releases large amounts of K-rich particles in the submicron size fraction (Ryu *et al.*, 2004).

## Conclusions

The mass size distributions for the atmospheric particles and water-soluble ionic species were measured using a cascade impactor in Iksan, Korea in spring, summer, and fall-winter of 2005. Ion chromatography was used to analyze for the water-soluble inorganic components. The effects of Asian dust on the airborne particles in conjunction with their episodes with higher particulate concentrations were also examined in terms of the size distribution of water-soluble inorganic ion species. Average fine and coarse mass concentrations of atmospheric particles were, respectively, 31.4 and 82.6  $\mu\text{g m}^{-3}$  in spring and 35.8 and 73.4  $\mu\text{g m}^{-3}$  in fall-winter during the sampling period of 2005, while measurements of 69.8 and 9.9 were obtained in the sampling period of summer. The mass size distribution for the atmospheric particles during the non-Asian dust period was generally bimodal, whereas during the Asian dust period coarse particles constituted a major portion of the total particulate matter due to

the long-range transport of soil dust particles from loess regions of the Asian continent.  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  were mainly distributed in fine particles while  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were in greater abundances in coarse particles.  $\text{NH}_4^+$  was found to mainly exist as ammonium sulfate in fine particles. Coarse mode nitrate was ascribed to the reaction of gas phase nitric acid with sea salt during the non-Asian dust period, but with soil particles during the Asian dust period.

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