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## SEASONAL VARIATION OF AEROSOL COMPOSITION AT CHEJU ISLAND, KOREA

GREGORY R. CARMICHAEL,\* YANG ZHANG,\* LI-LING CHEN,\*  
MIN-SUN HONG† and HIROMASA UEDA‡

\*Center for Global and Regional Environmental Research and Department of Chemical and Biochemical Engineering, University of Iowa, U.S.A.; †Department of Environmental Engineering, Ajou University, Korea; and ‡Department of Applied Mechanics, Kyushu University, Japan

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**Abstract**—A preliminary assessment of the seasonal variation in chemical composition of aerosols measured at Cheju Island, Korea, is presented. Weekly and monthly averaged aerosol composition derived from 15 months of daily filter measurements are presented. The annual-average non-sea-salt sulfate and nitrate mass concentrations of aerosols measured at Cheju are found to be  $6.9 \mu\text{g m}^{-3}$  and  $1.2 \mu\text{g m}^{-3}$ , respectively; calcium and potassium are present in nearly equal quantities at  $\sim 0.5 \mu\text{g m}^{-3}$ , and ammonium averaged  $1.4 \mu\text{g m}^{-3}$ . Each species is found to follow a seasonal cycle with sulfate, nitrate, ammonium, potassium and calcium all showing up to 50% higher values in the spring. In contrast, chlorine is 30% lower in the spring. Aerosol enrichment factors relative to the composition of seawater and crustal material from the Gobi dust-source region in China are also presented. The aerosol measured at Cheju is found to be enriched in sulfate, nitrate and ammonium, but deficient in chlorine (relative to seawater). These results along with modeling studies suggest that the dust surfaces play an important role in nitrate and sulfate formation. Copyright © 1996 Elsevier Science Ltd

*Key word index:* Aerosols, enrichment factors, dust, aerosol modeling.

### 1. INTRODUCTION

The characterization of East Asia atmospheric aerosols is the focus of this paper. Of particular interest is the springtime. Spring in East Asia is a period of high aerosol loading caused by frequent dust-storm events. Asian dust (also called Kosa or Yellow Sand) is up-lifted into the middle troposphere by low-pressure systems and transported thousands of kilometers over East China, Korea, Japan, and out into the Pacific Ocean (Kotamarthi and Carmichael, 1993). These storms are initiated by strong winds and travel behind cold fronts and occur most frequently during March, April and May (Uematsu *et al.*, 1983). The spring dust storms contribute to a number of environmental effects in the region including visibility impairment, mineral deposition to the coastal zones, and elevating the pH of precipitation.

In this paper, aerosol measurements at Cheju Island, Korea, are presented and discussed. Fifteen months of data on the chemical composition of aerosols obtained from tape-sampler filters are presented along with an analysis of seasonal cycles and enrichment factors to provide a preliminary look at the aerosol composition in the region. Model calculation of the interaction between the ambient aerosols and the tropospheric chemical cycles are also presented and used in the interpretation of the observations.

### 2. OBSERVATIONS

#### 2.1. Description of the Cheju site

Cheju Island is an ideal location to monitor the atmospheric chemistry of East Asia (see Fig. 1). Cheju is a volcanic island with peak elevation of  $\sim 2000$  m, and is a major resort area with no large industrial sources. The island is located in the East China Sea,  $\sim 100$  km south of the Korea mainland,  $\sim 250$  km west of Kyushu, Japan,  $\sim 500$  km east-northeast of Shanghai, China, and  $\sim 1000$  km north-northeast of Taipei. The measurement site is located in an area called Kosan on the far western edge of the island.

Seasonal meteorological conditions at Cheju (presented in Table 1) are such that the air mass trajectories reaching Cheju Island vary distinctly with season. In late winter, the flows are from the north and the Cheju site sample air masses influenced by North and South Korea; in spring, the flows are from the northern half of China under the influence of the anthropogenic activities and Asian dust storms; in summer, the flows are from the south-southeast with air-mass characteristics representing activities in southern China and Taiwan, Pacific maritime conditions, and southern Japan, respectively; while in the fall, the flows are from the east-northeast with characteristics of the emissions of Japan and Korea. Thus, during all seasons, the Cheju site monitors air masses impacted

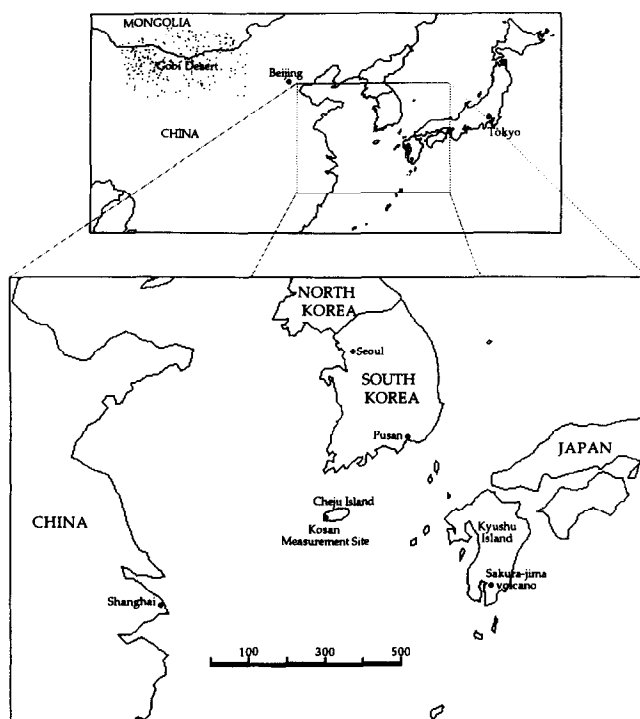


Fig. 1. Description of Cheju site.

Table 1. Meteorological parameters at Cheju Island, Korea

Month	Wind speed ( $\text{m s}^{-1}$ )	Wind direction	Temperature ( $^{\circ}\text{C}$ )	Total precipitation (mm)	RH (%)
92-Feb.	7.7	N	6.9	159.0	71.0
Mar.	5.0	N-NE	10.1	134.4	78.0
Apr.	5.2	N-NNE; SE	13.7	115.4	77.6
May	4.2	NNW-NNE; S-SE	16.4	96.5	79.5
Jun.	3.5	N-ENE; SSE-SE	19.7	76.1	82.8
Jul.	3.5	SSE-S	26.0	92.0	91.1
Aug.	3.2	SSE-SE; N-NNE	26.1	326.6	84.5
Sep.	6.8	SSE-SE; N-NNE	23.1	133.6	79.6
Oct.	6.2	NNW-NNE	17.4	4.0	74.0
Nov.	6.7	N-NNE	12.6	56.6	71.0
Dec.	13.8	N	9.7	33.9	73.0
93-Jan.	11.5	N-NNE	5.4	32.8	73.5
Feb.	10.4	N	7.1	66.6	75.8
Mar.	7.9	NNW-N	8.9	90.7	74.9
Apr.	7.4	NNW-N; SE	12.5	23.6	73.8
May	6.3	NNW-N; SE	16.4	132.3	82.8

by anthropogenic activities. In addition, the fuel and industrial characteristics of each country in the region are quite different, and these differences should lead to different aerosol characteristics. The peak precipitation rates occur in early spring and late summer.

Measurements at Cheju Island began in 1991 with cooperation between Ajou University, South Korea; Kyushu University and the National Institute for Environmental Studies (NIES), Japan; University of

Iowa; NOAA; KIST (Korea Institute for Science and Technology); and the University of Miami. A permanent measurement site was established on the western edge of Cheju Island (near Kosan) on the grounds of a meteorological station. A small measurement laboratory was constructed and NOAA provided (loaned) chemical analysis equipment for  $\text{NO}-\text{NO}_x$ ,  $\text{SO}_2$  and ozone, University of Miami provided a Hi-Vol aerosol sampler, and Japan-NIES provided an aerosol

tape sampler. The NOAA equipment was used for gaseous monitoring from September 1991 through March 1993. The NOAA instruments have subsequently been replaced by instruments purchased by the Environmental Research Center at the Korean Institute for Science and Technology, and by Japanese Institutes. Complete meteorological information (i.e. wind-speed direction, temperature, relative humidity, radiosonde data, precipitation, etc.) is available at this site.

## 2.2. Sampling and analysis

Beginning in March 1992, aerosols have been collected using a Kimoto High Volume Tape Sampler (Model 400EL). Air is sampled continuously through polytetrafluoroethylene (PTFE) filters at a flow rate of 150–180 l min<sup>-1</sup> from a sampling probe mounted on top of the measurement laboratory (need height info). The normal operation is that 24-h samples are taken. However, 6-, 12- and 48-h samples are also collected.

The filters are analyzed for Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. The chemical analysis consisted of extraction with water, shaking for 30 min, followed by filtration using a 0.45 μm cellulose acetate membrane. The filtrate was then analyzed for Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> using capillary electrophoresis; Ca<sup>2+</sup> and Mg<sup>2+</sup> using inductively coupled plasma atomic emission spectrophotometry; Na<sup>+</sup> and K<sup>+</sup> using atomic absorption spectrophotometry; and NH<sub>4</sub><sup>+</sup> using UV-VIS spectrophotometry. Data from these filters are the focus of this paper.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Aerosol composition and seasonal cycles

The aerosol composition at Cheju from March 1992 through May 1993 is summarized in Fig. 2 (please note that June is missing for most species due to a technical problem). Presented are the weekly averages calculated from the analyzed individual daily filters (~293 filters). Shown in Fig. 3 are the monthly averages (prepared from the daily filters), presented in terms of polar plots. In general, all species show a seasonal cycle. For example, calcium shows a seasonal cycle with peak values in the spring, reflecting the transport of Yellow Sand from northern China during this season. Nitrate also shows a strong seasonal cycle with peak values in the spring. Non-sea-salt (NSS) sulfate and ammonium concentrations show a similar seasonal cycle, but with summertime values remaining somewhat elevated. In terms of a general classification, it is found that Ca<sup>2+</sup>, K<sup>+</sup>, and NO<sub>3</sub><sup>-</sup> tend to be maximum in spring; SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> tend to be maximum in late spring–early summer; and Na<sup>+</sup>, Cl<sup>-</sup> and Mg<sup>2+</sup> peak in the winter. Monthly averages of sulfate and ammonium range from 3 to 8 μg m<sup>-3</sup> and 1 to 2 μg m<sup>-3</sup>, respectively. Nitrate values are typically lower (by a factor of 5–7) than sulfate.

The seasonal cycles largely reflect changes in the wind direction. As discussed previously, the wind flow conditions at Cheju show a seasonal cycle with winter season flows predominantly from the northeast, and changing to north-northwesterly during the spring. During the summertime, the flow direction is generally south to southeasterly, and changes in the fall to east-northeasterly winds. In general, the aerosols show high concentrations during conditions where the flow is from the northerly directions and minimum values when the flows are southerly. Sulfate and ammonium ions show the same general behavior, but their values remain quite high throughout the year. The elevated sulfate levels in July under conditions of southeasterly flows may be due to emissions of SO<sub>2</sub> from the Sakura-jima volcano located in southern Kyushu and the summer ammonium values may reflect the strong temperature dependency in NH<sub>3</sub> emissions. In addition, late summer and early fall are the wettest seasons and this also contributes to the summer minimum.

Further insights into the aerosol chemistry at Cheju Island are illustrated by examining averages and ratios of the chemical species. The annual average composition of the aerosol measured at Cheju, derived from daily tape-filters, is presented in Table 2. The annual-average NSS sulfate and nitrate mass concentrations are 7.0 μg m<sup>-3</sup> and 1.2 μg m<sup>-3</sup>, respectively. Calcium and potassium are present in nearly equal quantities at ~0.5 μg m<sup>-3</sup>, while ammonium averages 1.4 μg m<sup>-3</sup>. The annual mean mass ratios are: SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> = 6.0; NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> = 0.2; Ca<sup>2+</sup>/Na<sup>+</sup> = 0.3; and NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup> = 1.2. Also shown in Table 2 are the averages for the spring periods (March–April–May). Calcium and nitrate concentrations are 40–50% higher while sulfate and ammonium are ~10% higher in the spring. Sulfate, nitrate, ammonium, potassium and calcium, all show higher values in the spring. In contrast, chlorine is 30% lower in the spring.

These ratios can be compared to other aerosol measurements in Japan and Korea. For example, Nishikawa *et al.* (1991) have measured aerosol during spring months at Yaku Island (south of Kyushu Island, ~500 km southeast of Cheju). They found SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> ratios of ~6 and NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> ratios of ~0.05 during long-range transport events, and values of 2 and 0.2, respectively, during other periods. Kang and Sang (1991) analyzed aerosol measurements in the greater Seoul area and found annual averages of SO<sub>4</sub><sup>2-</sup>/NO<sub>3</sub><sup>-</sup> ~4 and NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> ~0.1. Also, Mukai *et al.* (1990) analyzed monthly filters taken at Oki Island, Japan, located in the Sea of Japan, 90 km north of the southern part of Honshu, and ~700 km west-northwest from Cheju. The annual average composition (based on five years of data) of the aerosol is: SO<sub>4</sub><sup>2-</sup> = 3.6 μg m<sup>-3</sup>; NO<sub>3</sub><sup>-</sup> = 0.1 μg m<sup>-3</sup>; NH<sub>4</sub><sup>+</sup> = 0.5 μg m<sup>-3</sup>; Ca<sup>2+</sup> = 0.15 μg m<sup>-3</sup>; K = 0.13 μg m<sup>-3</sup>; and Na<sup>+</sup> = 0.4 μg m<sup>-3</sup>. These values are all lower than those found at Cheju. The

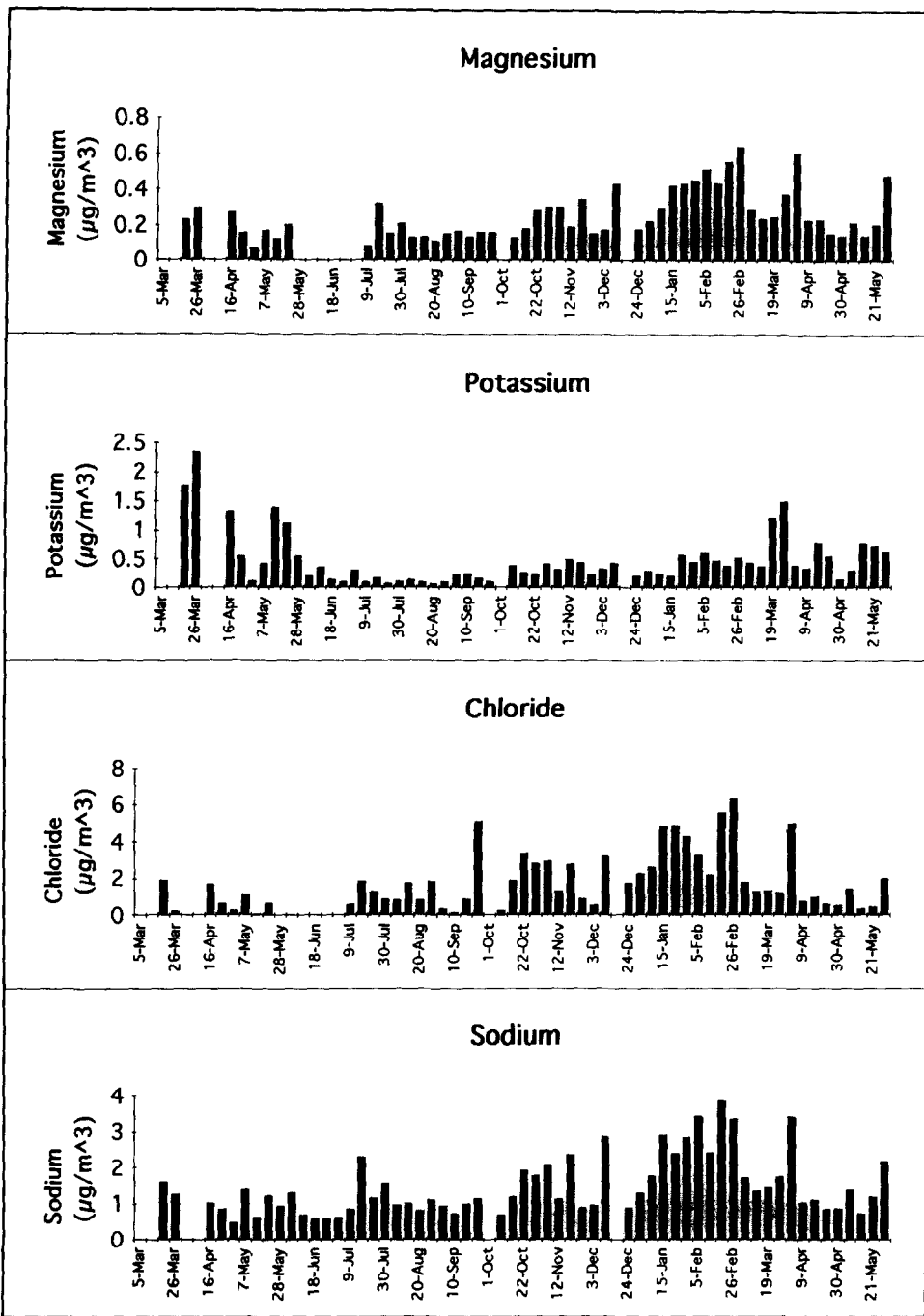


Fig. 2. Weekly average composition of aerosols at Cheju determined from the tape-filters.

seasonal cycles are very similar as is the mean  $\text{NH}_4^+/\text{SO}_4^{2-}$  (0.16, mass basis). The nitrate value is a factor of 9 lower at Oki and the reason for this is unclear.

Aerosol enrichment factors relative to the composition of seawater and crustal material from the Gobi dust-source region in China are summarized in Table 3. The enrichment factors relative to seawater show that the aerosol measured at Cheju is enriched in

sulfate, nitrate and calcium. The enrichment factor for chlorine (relative to seawater) is lower than 1. This suggests that chemical reactions which liberate sea-salt chlorine may be occurring on the aerosol particles during their transport to Cheju. Possibilities include sea-salt reactions with nitrogen oxides and/or ion-exchange reactions with strong acids (Finlayson-Pitts, 1993; Robbins *et al.*, 1959). The enrichment factors show a rather weak seasonal variation. All the species

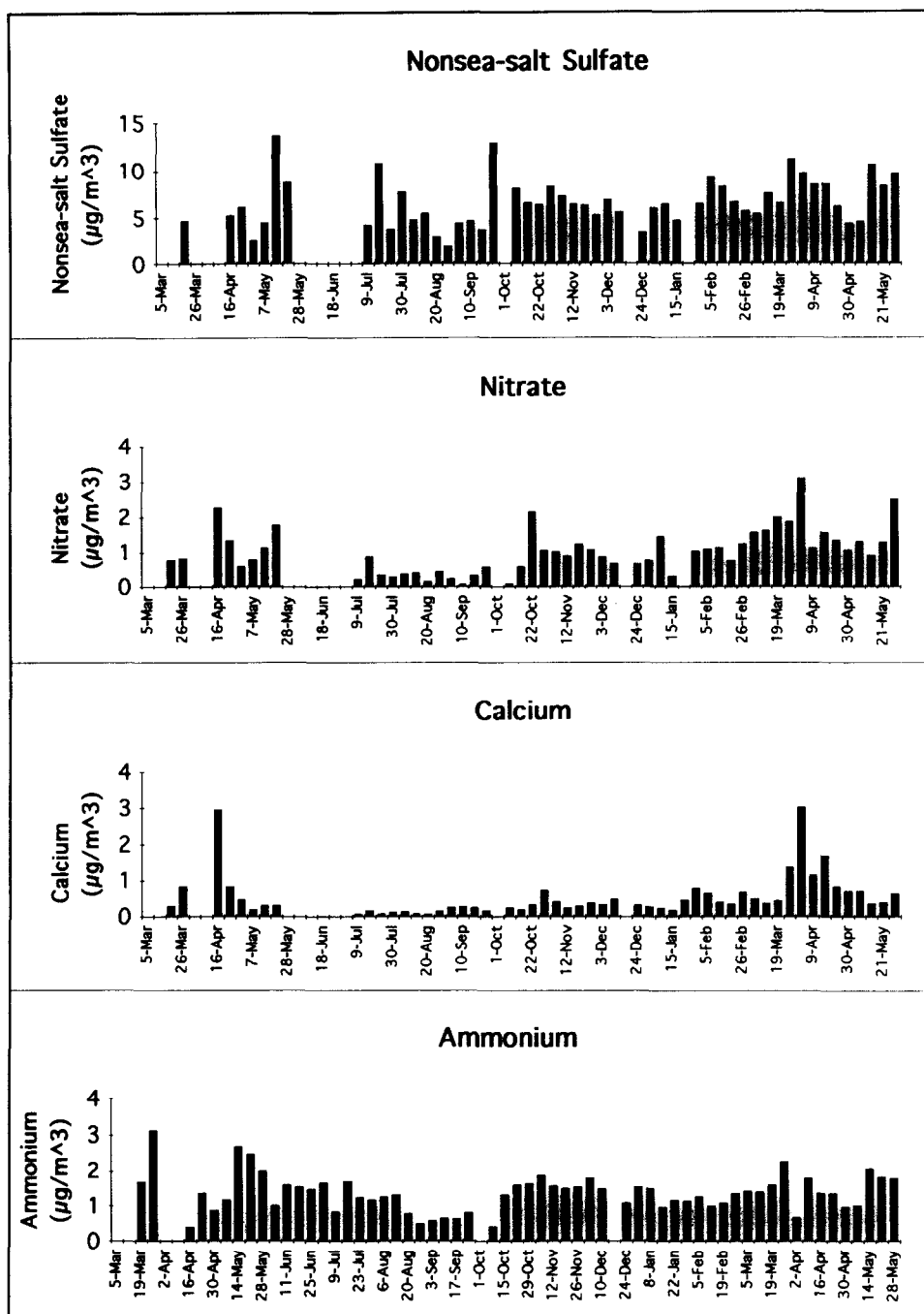


Fig. 2. (Continued).

except chlorine and magnesium show higher enrichment factors relative to seawater during the spring. In the case of chlorine the enrichment factor is lower during the spring months, suggesting more active chlorine-releasing gas-solid reactions during this time period.

Enrichment factors relative to the composition of crustal material in the source regions of Asian dust (northern China) are also presented in Table 3. Typically, enrichment factors relative to crustal materials

are based on ratios with aluminum. However, the tape-filters were not analyzed for aluminum. Thus, in this study, enrichment factors were calculated based on calcium ratios. Sulfate, ammonium and nitrate, all show enrichments relative to soil composition. In contrast, magnesium and potassium ratios suggest that they are largely of crustal origin.

Particulate sulfate and nitrate are not associated with the mineral dust at the source regions where the desert soils contain few calcium salts besides calcium

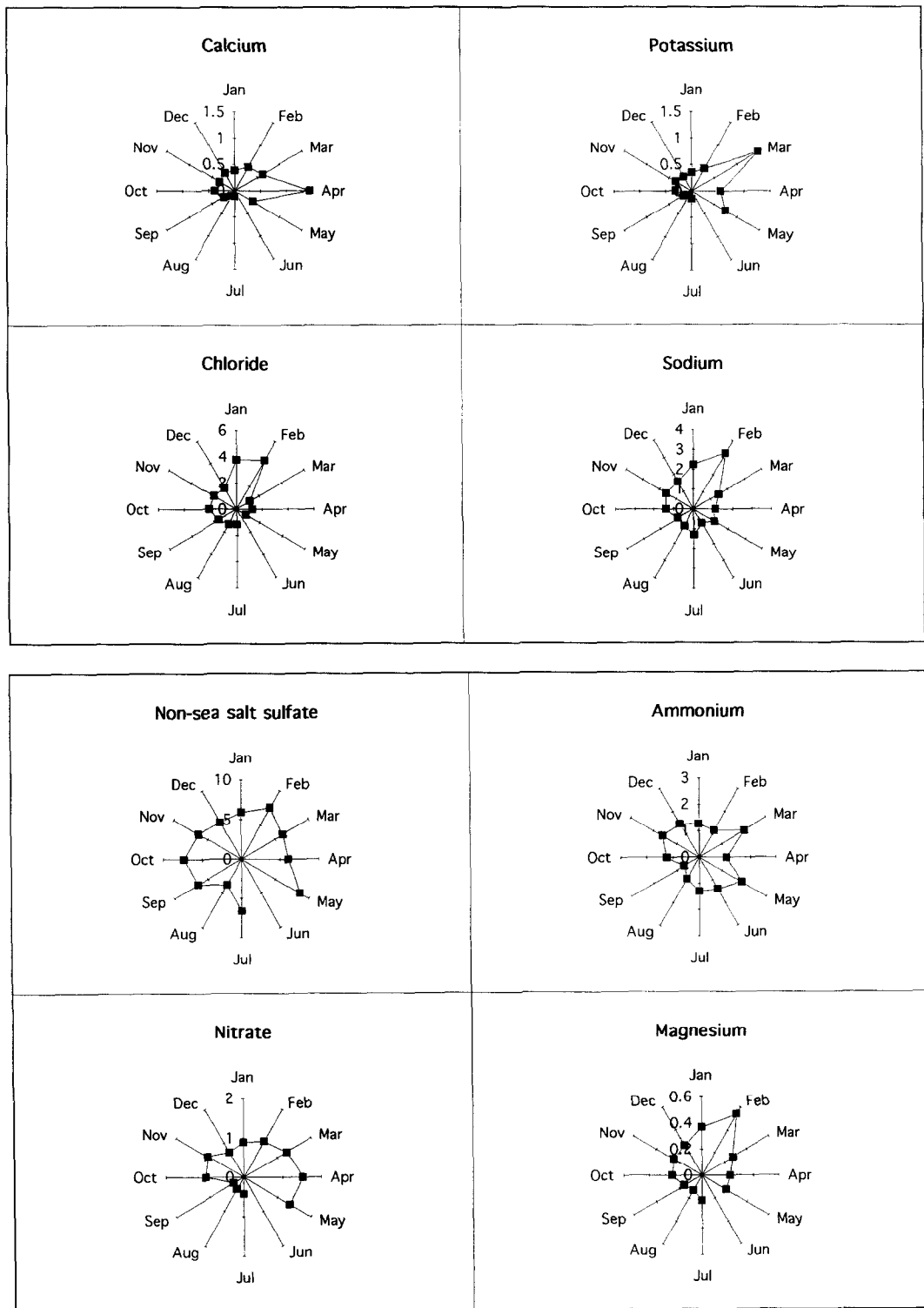


Fig. 3. Monthly average aerosol composition (in  $\mu\text{g m}^{-3}$ ) determined from daily tape-filters.

carbonate (Inoue and Yoshida, 1990; Nishikawa *et al.*, 1991). Yet elevated sulfate and nitrate levels are found on aerosols as far away as in the central Pacific Ocean (Prospero and Savoie, 1989; Savoie and Prospero,

1989). Microscopic analysis has shown that Asian dust particles consist of irregularly shaped insoluble cores covered with a layer of soluble substances (Okada *et al.*, 1987). In the source areas, the soluble

Table 2. Aerosol composition at Cheju Island, Korea, March 1992–May 1993, in  $\mu\text{g m}^{-3}$ 

	Ca <sup>2+</sup>	Na <sup>+</sup>	nssSO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>
Spring average	0.8	1.4	7.9	1.6	1.4	1.5	0.6	0.3
Annual average	0.5	1.7	6.9	1.2	1.9	1.4	0.4	0.3

Table 3. Aerosol crust and seawater enrichment factors (E.F.) calculated from tape-filter data at Cheju Island, Korea, March 1992–May 1993 (Gobi soil data from Nishikawa (1993))

	Crust E.F.		Seawater E.F.	
Na/Ca	8.3	SO <sub>4</sub> /Na	16.3	
nssSO <sub>4</sub> /Ca	7165.4	Cl/Na	0.6	
NO <sub>3</sub> /Ca	977.4	NO <sub>3</sub> /Na	67765.0	
Cl/Ca	1933.5	Mg/Na	1.4	
NH <sub>4</sub> /Ca	1766.3	Ca/Na	8.3	
K/Ca	2.3			
Mg/Ca	2.9			

material is carbonate but, farther from the source areas, the sulfates and nitrates are the major constituents. Hirai *et al.* (1991) proposed that sulfate and nitrate are sorbed and/or formed on the surfaces of wetted dust particles, and displace the carbonates. Chemical composition of precipitation sampled during dust events in Korea and Japan are consistent with this hypothesis and show that up to 75% of the carbonate is displaced by nitrate and sulfate by the time the particles reach Korea and Japan (Hirai *et al.*, 1991).

### 3.2. Modeling analysis

The above results suggest that species such as sulfate and nitrate become associated with the aerosol during the transport processes. This indicates that interactions between wind-blown dust and chemical processes involving gas-phase species play an important role in determining the aerosol composition in East Asia. To investigate these issues further, a modeling study was initiated.

The interactions between dust and the trace gas cycles were studied by use of a box model which treats the aerosol and the gas-phase chemical processes in a coupled manner. The box model is constructed from the STEM-II regional-scale transport/chemistry/removal model (Carmichael *et al.*, 1991). The gas-phase chemical mechanism consists of 86 chemical species and 185 gas-phase reactions. The mechanism is based on that of Lurmann *et al.* (1986) and modified to include low NO<sub>x</sub> conditions and explicit treatment of isoprene. The rate coefficients for gas-phase nitrogen chemistry and reaction involving H<sub>x</sub>O<sub>y</sub> (representing OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>) species have been up-

dated based on recent studies (Atkinson *et al.*, 1982; Mckeen *et al.*, 1991; DeMore *et al.*, 1992). The aerosol mechanism includes dynamic and thermodynamic equilibrium processes and heterogeneous chemistry occurring on the surface of particle. Six trace species (i.e. NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>) are allowed to undergo surface reactions. Sulfate and particulate nitrate are allowed to form on the dust surface via a series of heterogeneous pathways (Luria and Sievering, 1991; Mamane and Gottlieb, 1989). Complete details are presented in Zhang *et al.* (1994).

The dust particles are modeled as a multicomponent aerosol using a log-normal size distribution formulation. A typical observed Asian dust distribution (Nishikawa, 1993) is used in the analysis. The size distribution is shown in Fig. 4 and is the one measured at Yaku Island, Japan. Yaku is a small island located ~ 50 km south of Kyushu Island. The distribution is divided into five aerosol size modes: 0.1  $\mu\text{m} < D < 0.5 \mu\text{m}$ ; 0.5  $\mu\text{m} \leq D < 1.5 \mu\text{m}$ ; 1.5  $\mu\text{m} \leq D < 6.0 \mu\text{m}$ ; 6.0  $\mu\text{m} \leq D < 20 \mu\text{m}$ ; and 20  $\mu\text{m} \leq D < 40 \mu\text{m}$ , where  $D$  denotes the diameter of a single particle in each bin. Each size mode is characterized by a single mean diameter for all the particles which have the size range between the specified upper and lower limits on the bins. The peak in the mass distribution occurs around 7  $\mu\text{m}$ .

Both coagulation and condensation processes are considered in the analysis. The discrete form of the coagulation equation is used (Gelbard and Seinfeld, 1980), and the coagulation coefficients are determined based on the Fuchs (1964) formulation. A set of semi-empirical equations based on the work of Hanel (1976) are used to account for changes in the size and mass of particles due to the condensation and evaporation of water vapor on the particle surface. For the range of relative humidity (RH) of 0–95%, the particle radius and mass are given as an explicit function of RH, mass-increase coefficient, as well as densities of dry particles and pure water. Since there is no measured data on the mass-increase coefficient of dust particles from the Gobi and Taklamakan Deserts, the relationships between mass-increase coefficient and RH for condensation and evaporation processes were interpolated based on the measurements of maritime aerosol over the Atlantic containing Saharan dust during 16–25 April 1969 (Hanel, 1976). The calculated dust mass distribution after 2 days of transport is presented for comparison with the observed distribution in Fig. 4. The modeled distribution is very similar to the observed distribution.

## Mass Distribution of Dust Particles

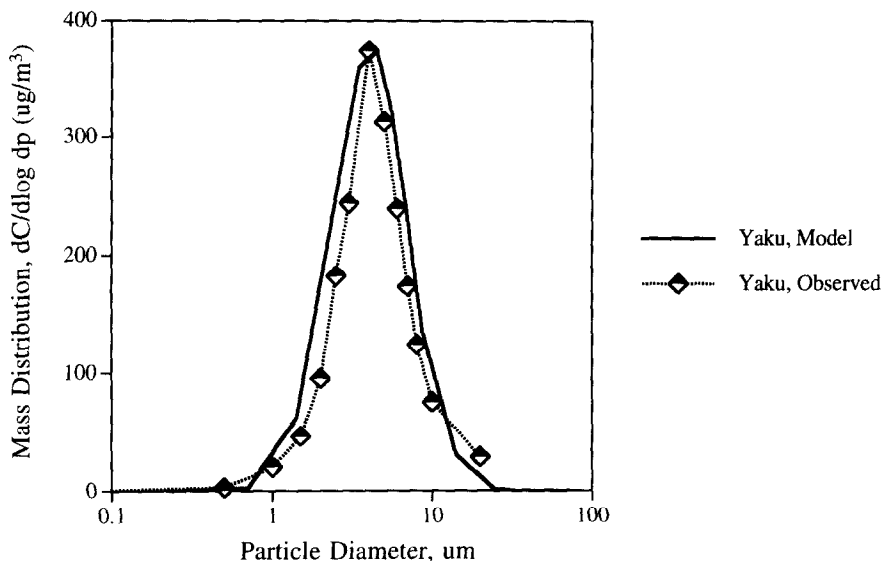


Fig. 4. Dust-size distribution. The observed distribution is at Yaku Island, Japan (Nishikawa, 1993).

This model was used to explore the interactions between dust and the photochemical oxidant cycle as air parcels are transported in the mid-troposphere from Northeast China to Cheju. We assume that dust and air with specific compositions are mixed together inside a well-mixed parcel, and the parcel is then transported as a closed system. Multiday simulations (each simulation is run for up to 5 days and begins at 8:00 local standard time (LST)) are performed to reflect typical transport times from China to Cheju. Ambient conditions are set to be representative of those encountered by air masses as they travel over East Asia to Cheju during springtime dust storms. We assume a parcel height of 4 km, a temperature of 283 K and a relative humidity of 80%. These values are selected from observations taken at Cheju. The initial chemical compositions used in the simulations are based on observations and are summarized in Table 4. An accommodation coefficient of 0.1 was used for all species based on recent measurements (Mozurkewich, 1986; Mozurkewich *et al.*, 1987; Gardner *et al.*, 1987; Van Doren *et al.*, 1991) and modeling studies (Chameides and Davis, 1982; Dentener and Crutzen, 1993; Li *et al.*, 1993). Simulations were performed with diurnal variation in the solar actinic flux. The initial dust loading was assumed to be  $100 \mu\text{g m}^{-3}$ .

Calculated particulate sulfate and nitrate as a function of travel time is presented in Table 5. Under typical transport times (3 to 5 days) from central China to Cheju 6 to  $12 \mu\text{g m}^{-3}$  of sulfate and 1.5 to  $2 \mu\text{g m}^{-3}$  of nitrate are produced. These values are consistent with the observations at Cheju (see Fig. 2).

Table 4. Summary of conditions used in the model simulations at Cheju

Components	Values
NO, ppbv	3.75
NO <sub>2</sub> , ppbv	1.25
HNO <sub>3</sub> , ppbv	0.0005
NH <sub>3</sub> , ppbv	1.0
SO <sub>2</sub> , ppbv	8.0
SO <sub>4</sub> , ppbv	1.0
O <sub>3</sub> , ppbv	50
NMHCs, ppbv	56.1
CO, ppbv	150
Dust, $\mu\text{g m}^{-3}$	100
Relative humidity, %	80
Temperature, K	283
Accommodation coefficient	0.1

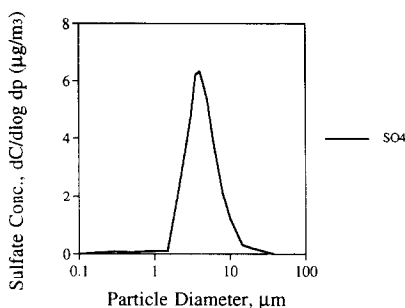
Table 5. Model calculated sulfate and nitrate concentrations (in  $\mu\text{g m}^{-3}$ ) as a function of travel time

Day	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>
3	6.1	1.7
4	8.7	2.1
5	11.6	2.2

In addition, the S to N mass ratios in the modeled aerosol vary from 4 to 5. These numbers are consistent with the S to N mass ratios in the anthropogenic emissions from China. For example Akimoto and



## Mass Distribution of Particulate Sulfate at Cheju



## Mass Distribution of Particulate Nitrate at Cheju

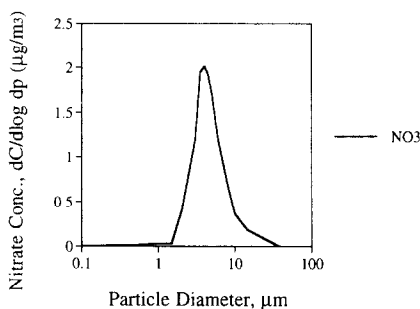


Fig. 5. Predicted sulfate and nitrate aerosol concentrations as a function of size.

Narita (1994) estimate that the S to N mass ratios in the emissions for surrounding countries vary from 5 for China, 2 for South Korea, and 0.6 for Japan. Cheju local emissions range from 1 to 2.

Model-predicted aerosol sulfate and nitrate are shown as a function of size in Fig. 5. These model results provide insights into the mechanisms which influence the chemical composition of the aerosol. Aerosol sulfate is formed through two major pathways. Submicron particles are generated by homogeneous and heterogeneous nucleation and these particles add mass to the small end of the distribution. These particles also coagulate with pre-existing dust particles. Sulfate is also produced on the surface of the wetted dust particles through reactions with peroxide and other available oxidants. These processes lead to the size distribution shown in Fig. 5 and a bi-model number distribution (not shown).

The mechanism of particulate nitrate formation is different under daytime and nighttime conditions. During the daytime, the gas-to-particle conversion of  $\text{HNO}_3$  via the production of nitric acid in the gas phase followed by deposition to the dust surface is the dominant mechanism. In contrast, during the nighttime, the conversions of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  on the wetted aerosol surface dominate total nitrate formation. The particulate nitrate formation rate is a function of aerosol size and number density. These quantities

influence both the available surface area for reaction and the effective diffusion rate of the precursors to the surface. For the given size distribution of dust, the available surface area and effective mass transfer rates results in the peak nitrate levels being associated with dust particles which are a few microns in size.

These studies support the idea that sulfate and nitrate become associated with the dust during the long-range transport processes. These chemical processes producing strong acids could also account for the displacement of chlorine from the dust that is observed in the enrichment factors relative to seawater.

## 4. SUMMARY

The seasonal variation in chemical composition of aerosol measured at Cheju Island, Korea was presented. The annual-average NSS sulfate and nitrate mass concentrations were found to be  $7.0 \mu\text{g m}^{-3}$  and  $1.2 \mu\text{g m}^{-3}$ , respectively. Calcium and potassium were present in nearly equal quantities at  $\sim 0.5 \mu\text{g m}^{-3}$ , while ammonium averaged  $1.4 \mu\text{g m}^{-3}$ . The annual-mean mass ratios were:  $\text{SO}_4^{2-}/\text{NO}_3^- = 6.0$ ;  $\text{NH}_4^+/\text{SO}_4^{2-} = 0.2$ ;  $\text{Ca}^{2+}/\text{Na}^+ = 0.3$ ; and  $\text{NH}_4^+/\text{NO}_3^- = 1.2$ . Each species was also found to follow a seasonal cycle. Sulfate, nitrate, ammonium, potassium and calcium, all showed higher values by up to 50% in the spring. In contrast, chlorine showed a 30% decrease in the spring. Aerosol enrichment factors relative to the composition of seawater and crustal material from the Gobi dust-source region in China were also analyzed. The enrichment factors showed that the aerosol measured at Cheju is enriched in sulfate, nitrate and ammonium, while that for chlorine (relative to seawater) is lower than 1. While the concentrations of most species showed higher levels in the spring, the enrichment factors were found to be only slightly higher in the spring. These observations are based on a rather short time record. Clearly, a longer measurement record is needed to establish more completely the seasonal cycle of aerosol composition at Cheju.

These results do suggest that dust surfaces play an important role in nitrate and sulfate formation. The influence of dust on the formation of particulate nitrate and sulfate was studied using a combined aerosol/gas-phase chemistry model. Dust was found to provide an important surface for aerosol nitrate and sulfate formation. Under typical transport times (3 to 5 days) from central China to Cheju, 6 to  $12 \mu\text{g m}^{-3}$  of sulfate and 1.5 to  $2 \mu\text{g m}^{-3}$  of nitrate are produced. These model results are consistent with the observational data and lend support to the hypothesis that dust-gas-phase interactions is an important process.

Dust is a very important trace species throughout Asia (and in many other regions around the world) and its role in tropospheric chemistry needs to be better understood. Further work which couples the large-scale dynamic transport processes with the

small-scale surface/gas-phase interactions is required to better quantify the role of dust in tropospheric chemistry.

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