



SUMMERTIME CHARACTERISTICS OF AEROSOL COMPOSITION AT CHEJU ISLAND, KOREA

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Abstract—To understand the characteristics of air quality during summer in Northeastern Asia, an intensive field study had been carried out at Cheju Island, Korea during the period of 20 July to 10 August 1994. Total suspended particles and PM_{2.5} particles were collected and their mass and ion concentrations were analyzed. Along with PM_{2.5}, gaseous species were collected on impregnated filters. Also, another low volume sampler collected carbonaceous species analysis. The sampling period could be classified into two distinctive periods, with a highly polluted period between 20 July and 1 August and an unpolluted period between 2 and 10 August. During the polluted period, the mean non sea-salt sulfate concentrations in TSP and PM_{2.5} were 16.6 and 13.4 μg m⁻³, respectively. Backward trajectory analysis showed that air parcels arriving at the sampling site during the former period were mainly from Korea and Japan while air parcels during the latter period were from the North Pacific Ocean. It was suggested that the air pollutant levels during the latter period could be considered as marine background concentrations in the region during summer. © 1998 Elsevier Science Ltd. All rights reserved

Key word index: PM_{2.5}, TSP, ions, carbonaceous species, marine background concentrations.

1. INTRODUCTION

At present more than one-third of the world population live in Northeastern Asia with high air pollutant emissions. Emissions of SO₂ in the late 1980s in the region (about 15,000 GgS yr⁻¹) were far higher than those of the United States of America (about 10,000 GgS yr⁻¹) (Kim *et al.*, 1997a). As shown in Fig. 1, Cheju Island is located at the northern part of the East China Sea, and surrounded by China, Korean peninsula, and Japanese Islands to west, north, and east, respectively. Cheju Island is one of the cleanest areas in Korea with emissions of about 1% of total Korean emissions of SO₂ and NO_x. Thus, Cheju Island is an ideal place to monitor the long-range transport of air pollutants in the region.

A few monitoring studies had been carried out at Cheju Island (Arimoto *et al.*, 1996; Carmichael *et al.*, 1996; Kim *et al.*, 1995, 1996, 1997a,b). However, those studies had focused either on monitoring of air pollutants during spring and winter or routine measurement of water soluble ion concentrations of

total suspended particles (TSPs). No intensive measurement has been carried out during summer. The prevailing winds in the regions except summer are from west or northwest while the prevailing winds during summer are from south or southwest (Carmichael *et al.*, 1996; Kang *et al.*, 1993). Monitoring studies made during spring or winter has been, thus, aimed at monitoring the long-range transport of air pollutants from Asia continent to the Pacific. Thus, during summer, it is expected that the characteristics of the long-range transport of air pollutants in the region be different from those in other seasons.

Also no measurement of carbonaceous species in aerosol has been reported yet. Main sources of elemental carbon (EC) are combustion sources. Since chemical transformations of elemental carbon in ambient conditions are limited, EC is a good indicator of primary anthropogenic air pollutants. Organic Carbon (OC) species in aerosol can be either emitted from primary emission sources or generated from chemical reactions among primary gaseous organic carbon species in the atmosphere. In the polluted urban area, carbonaceous species contribute to approximately 10–20% of TSP mass and 40% of fine particle mass (Baik *et al.*, 1996; Macias *et al.*, 1981). In remote ocean areas, OC and EC contribute to approximately 11 and 0.3% of fine particle mass, respectively

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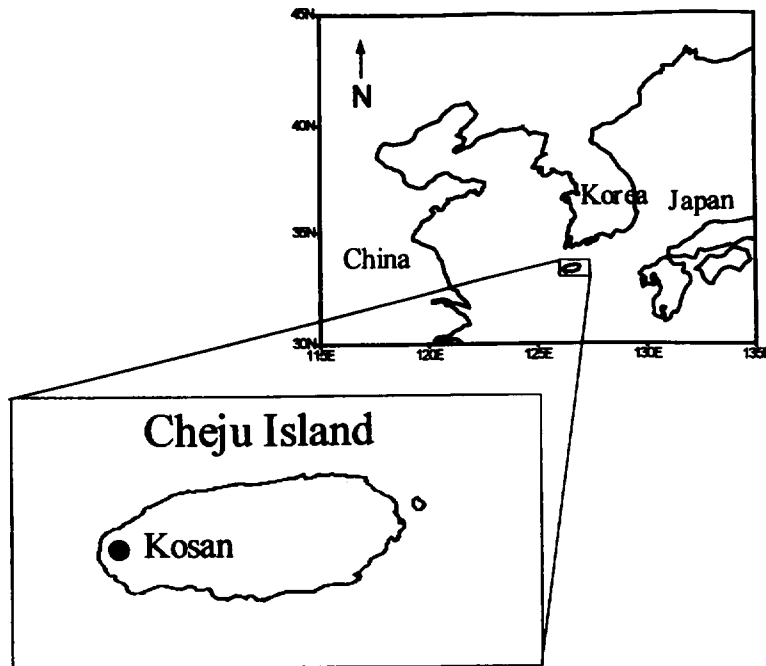


Fig. 1. The map of Cheju Island and surrounding area.

(Heintzenberg, 1989). Therefore, to understand the characteristics of air pollutants measured in Cheju Island, it is important to measure both EC and OC in aerosol.

Global Environmental Research Center at Korea Institute of Science and Technology (KIST) has carried out an intensive field monitoring study during the summer of 1994 to study the characteristics of air quality on Cheju Island during summer. In this paper, we present measurement results during the period and discuss aerosol characteristics based on the backward trajectory analysis of air parcels.

2. MEASUREMENT

The monitoring site was located at the western tip of Cheju Island, called Kosan ($126^{\circ} 10'E$, $33^{\circ} 17'N$). Samplers were installed about 20 m inside of a cliff, which was about 70 m above mean sea level (asl). TSPs, $PM_{2.5}$ particles, and gaseous species were collected.

Four high volume samplers (General Metal Works Inc.) were used sequentially to collect TSP. Each sampler collected particles for 6 h with the flow rate of about 920 l p min (LPM). Flow rate was recorded both on a strip chart and computer via pressure transducer (Dwyer, 602-4). Teflon-coated glass fiber filters (Pallflex) were used. Two $PM_{2.5}$ particle samplers were used to collect fine particles. Each $PM_{2.5}$ sampler consisted of four parts; a cyclone, a filter holder, a critical orifice, and a pump. Teflon coated alumi-

num cyclone with a cut size of $2.5 \mu m$ at the flow rate of 10 LPM (URG-2000-30EN) was used. The Teflon filter holder for 47 mm filters (Savillex-6T-47-4N) was used to minimize the sampling errors. A critical orifice with the flow rate of 10 LPM (BGI-SO-10) was used with a diaphragm pump (ULVAC-DA-20D) to control flow rate.

A three-stage filter holder was used for one $PM_{2.5}$ sampler to collect both fine particles and gaseous species. A Teflon filter (Gelman, Zefluor) was used at the first stage of the holder to collect fine particles. On the second and third stages, sodium carbonate and citric acid impregnated quartz fiber filters (Whatman, QM-A) were inserted to collect nitric acid and hydrochloric acid, and ammonia, respectively. Collection efficiency of gaseous species of a three stage filter pack was known to be not as high as that of a denuder (Appel *et al.*, 1988; Harrison and Kitto, 1990). Furthermore, in marine environment, nitric acid tends to be collected in particles on the filter due to acid-base interactions as will be discussed later. Therefore, the values reported in this paper for gaseous species should be considered as conservative values, i.e. lower limit values.

Another separate $PM_{2.5}$ sampler was used to collect fine particles for analysis of carbonaceous species. Quartz fiber filters (Whatman, QM-A) were heated at $850^{\circ}C$ for 90 min and then placed in clean polyethylene petridishes. The petridishes were then wrapped with Teflon tape and aluminum foil, and stored in a freezer until field measurement.

The sampling period was between 20 July and 10 August, 1994. Sampling started on about 0900 LST and lasted for 24 h except high volume samplers that were operated sequentially for 6 h. The TSP data reported in this paper were averaged for 24 h.

Analyses of water-soluble ions in fine particles and gaseous species were carried out by KIST while water-soluble

ions in TSP were analyzed by Cheju National University. At KIST, anions, SO_4^{2-} , NO_3^- , Cl^- , HNO_3 as NO_3^- , and HCl as Cl^- , were analyzed by an ion chromatography (DKK LIC-10), NH_4^+ and NH_3 as NH_4^+ by the indophenol colorimetric method (Diode Array 8541A), and other cations, Na^+ , K^+ , Ca^{2+} , and Mg^{2+} by an atomic absorption spectroscopy (Hitachi 8200). Due to the problems in the ion chromatography, the lower detection limits (LDLs) for anions were rather high as shown in Table 1. It caused interpretation of acidic gases difficult since most of these samples were below their LDLs. However, fine particle anion concentrations were, except sulfate during August, generally above the LDLs and, thus, interpretation on these anions could be made without losing accuracy. Accuracy of DKK LIC-10 was about 0.5 ~ 1.0% of the reported values depending on species. At the Cheju National University, the same methods were used with different analyzers (anions by Dionex DX-100, cations by Phillips SP9-800, respectively). Standard solutions for ion analysis

of both institutions were cross analyzed for quality assurance.

Analysis of carbonaceous species was carried out at AtmAA, Calabasas, CA, USA by the selective thermal manganese oxidation (TMO) method (Fung, 1990). The samples were shipped to AtmAA via express air mail in an ice-cooler with Blue-ice. Samples taken from the filter for carbon analysis were placed into the platinum boat with the particles in contact with the MnO_2 . Thirty microliters of 0.02 N HCl were added to the disks. The boat then advanced to the volatilization zone at 120°C, where CO_2 , water, and a small amount of volatile organics were removed and measured. Next, the samples were advanced to the furnace set at the optimum speciation temperature (525°C) for oxidation of OC. The final oxidation of EC took place at 850°C. The CO_2 resulting from each oxidation step was converted to methane for detection with a flame ionization detector. Compared to thermal-optical reflectance (TOR) method, this method can get comparable total carbon values and slightly lower EC

Table 1. Summary of aerosol and gas measurements at Kosan, Cheju Island during Summer, 1994 (unit: $\mu\text{g m}^{-3}$)

(a) TSP

Species	Overall mean	Standard dev. of the mean	Range	Mean \pm Standard of the mean dev.	
				July ^a	August ^b
Mass	56.12	6.24	28.83 ~ 117.45	66.84 \pm 28.83	38.69 \pm 5.03
SO_4^{2-}	12.10	2.05	2.34 ~ 31.32	17.81 \pm 2.06	2.83 \pm 0.18
Cl^-	3.16	0.09	0.03 ~ 7.16	1.09 \pm 0.61	6.51 \pm 0.29
NO_3^-	1.78	0.15	0.57 ~ 3.60	1.94 \pm 0.23	1.52 \pm 0.11
NH_4^+	0.89	0.23	0.03 ~ 3.20	1.41 \pm 0.29	0.05 \pm 0.01
Na^+	4.95	0.25	3.43 ~ 8.03	4.99 \pm 0.39	4.89 \pm 0.21
K^+	1.34	0.16	0.45 ~ 2.60	1.84 \pm 0.13	0.54 \pm 0.02
Ca^{2+}	0.54	0.04	0.22 ~ 0.91	0.58 \pm 0.06	0.48 \pm 0.03
Mg^{2+}	0.36	0.04	0.13 ~ 0.76	0.30 \pm 0.06	0.46 \pm 0.02
nss SO_4^{2-}	10.86	2.06	1.14 ~ 29.96	16.55 \pm 2.07	1.60 \pm 0.18
nss Cl^-	- 5.75	0.64	- 9.58 ~ - 1.26	- 7.88 \pm 0.32	- 2.29 \pm 0.23
nss K^+	1.17	0.16	0.30 ~ 2.41	1.66 \pm 0.14	0.36 \pm 0.01
nss Ca^{2+}	0.36	0.04	0.09 ~ 0.71	0.39 \pm 0.05	0.30 \pm 0.03
nss Mg^{2+}	- 0.23	0.02	- 0.39 ~ - 0.07	0.29 \pm 0.02	- 0.13 \pm 0.01

(b) $\text{PM}_{2.5}$

Mass	20.61	3.74	4.00 ~ 61.81	29.21 \pm 4.60	6.62 \pm 0.84
SO_4^{2-}	8.40	1.97	< 1.30 ~ 32.50	13.56 \pm 2.16	< 1.30
Cl^-	1.04	0.09	< 0.66 ~ 2.73	0.76 \pm 0.13	1.48 \pm 0.18
NO_3^-	0.89	0.24	< 1.30 ~ 3.24	0.10 \pm 0.10	2.16 \pm 0.19
NH_4^+	2.81	0.51	0.27 ~ 7.95	4.24 \pm 0.50	0.47 \pm 0.07
Na^+	0.54	0.04	0.28 ~ 1.02	0.47 \pm 0.04	0.66 \pm 0.06
K^+	0.24	0.02	0.13 ~ 0.56	0.28 \pm 0.03	0.17 \pm 0.01
Ca^{2+}	0.07	0.01	< 0.03 ~ 0.23	0.05 \pm 0.02	0.10 \pm 0.02
Mg^{2+}	< 0.03	—	< 0.03 ~ 0.09	< 0.03	< 0.03
OC	3.74	0.39	1.34 ~ 7.29	4.58 \pm 0.49	2.36 \pm 0.16
EC	0.27	0.05	0.02 ~ 0.79	0.38 \pm 0.06	0.08 \pm 0.02
nss SO_4^{2-}	8.26	1.98	- 0.26 ~ 32.32	13.44 \pm 2.16	< 1.30
nss Cl^-	0.06	0.10	- 0.90 ~ 0.89	- 0.08 \pm 0.14	0.22 \pm 0.05
nss K^+	0.22	0.02	0.11 ~ 0.53	0.27 \pm 0.03	0.14 \pm 0.01
nss Ca^{2+}	0.05	0.01	- 0.02 ~ 0.21	0.04 \pm 0.02	0.07 \pm 0.02
nss Mg^{2+}	< 0.03	—	- 0.07 ~ 0.01	< 0.03	< 0.03

(c) Gaseous species

HNO_3	< 1.32	—	< 1.32	< 1.32	< 1.32
HCl	< 0.66	—	< 0.66	< 0.66	< 0.66
NH_3	1.45	0.30	0.00 ~ 4.11	0.81 \pm 0.27	2.50 \pm 0.47

^aJuly: 20 July–1 August ($N = 13$)

^bAugust: 2–9 August ($N = 8$)

values (Chow *et al.*, 1993). Sampling artifacts for OC were not quantified in this study.

Backward trajectory analysis had been carried out for air parcels arriving at the sampling site. Upper air meteorological data at the site were measured twice a day, on 0900 and 2100 LST, respectively, by the Cheju upper air meteorological station. Since the sampling started 0900 LST and lasted for 24 h, the data on 2100 LST were considered as representing the air parcel for each sampling day. In addition, grid Point Values (GPV) data from Japanese Meteorological Administration were used for the analysis. Linear interpolation of 1 h interval was used for time and objective analysis using Barnes scheme was used for space interpolation with the radius of influence of 500 km. Trajectories up to 4 d prior to the time of interest at 700, 850, and 1000 hPa level were estimated.

The weather during the period could be divided into four patterns. Between 19 and 26 July, it was hot and clear with low wind speed. The average of daily mean wind speed was 4.6 m s^{-1} with the daily mean temperatures between 27.2 and 29.0°C. Between 27 July and 1 August two typhoons (Walt, T7 and Brendan, T11) had passed over the Island. However, their effects were small with the total precipitation of about 20 mm at the site. During 2 and 8, August hot and humid North Pacific anticyclone expanded to Cheju Island. The daily mean temperature was above 28.0°C and the mean wind speed was 5.9 m s^{-1} . Starting 9, August typhoon Doug (T13) was located at about 140 km west of Cheju Island and it rained heavily at the site with strong winds. Precipitations at the site were 13.6 mm and 67.7 mm on 9 and 10, August respectively. The daily mean wind speeds during the two days were 9.5 and 17.3 m s^{-1} , respectively.

3. RESULTS AND DISCUSSION

3.1. General characteristics

A summary of measurement results, the overall mean values, standard deviations of the mean, and ranges of daily average concentrations is given in Table 1. Also shown in Table 1 are non-sea-salt (nss) concentrations of ions based on sodium ion (for example, sulfate to sodium ratio of 0.252 was used based on sea water composition from Horne, 1969). Trends of mass, nss sulfate, EC, and OC concentrations are also shown in Fig. 2. In Table 2, concentrations of major species during the study period were compared with those at other remote and polluted areas.

The mass concentrations in TSP on 23 and 31 July and 9 August were high while those in $\text{PM}_{2.5}$ did not show elevated values. Also, major anthropogenic aerosol species concentrations were not high on 31 July and 9 August. During the measurement period, the mean wind speed were higher than 10 m s^{-1} on 31 July and 9 August. Thus, the high mass concentrations on 31 July and 9 August were mainly due to the wind-blown sea-salt particles. The daily sodium concentrations in both days were also high.

Notable characteristics of air pollutant levels shown in Table 1 are high concentrations of nss sulfate and high fraction of nss sulfate to total sulfate. The mean nss sulfate concentrations in TSP and $\text{PM}_{2.5}$ were 10.86 and $8.26 \mu\text{g m}^{-3}$, respectively, which were higher than those at remote marine areas

($0.5 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$, Heintzenberg, 1989). These are also higher than those reported in Japanese remote marine sites, $8.0 \mu\text{g m}^{-3}$ in TSP in Okinawa Island (Hatakeyama, 1993) and between 0.2 and $4.2 \mu\text{g m}^{-3}$ in TSP in Oki Island (Mukai *et al.*, 1990). The values for this study are also higher than those measured at the same site previously. The mean nss sulfate concentration in TSP measured at the same site by a high-volume sampler during the spring of 1994 was $8.3 \mu\text{g m}^{-3}$ (Kim *et al.*, 1997a) while that in PM_{1} at the same period was $3.8 \mu\text{g m}^{-3}$ (Kim *et al.*, 1995). Also, the average nss sulfate concentration in TSP during the summer of 1992 was approximately $4.7 \mu\text{g m}^{-3}$ (Carmichael *et al.*, 1996).

The fractions of nss sulfate to total sulfate for TSP and $\text{PM}_{2.5}$ were 90 and 99%, respectively. Thus, most sulfates in aerosol, especially in fine particles, were from non-sea-salts. Similar high numbers, above 90%, had been reported at the same site for fine particles (Kim *et al.*, 1996) and TSP (Carmichael *et al.*, 1996; Kim *et al.*, 1997a). Also, nss sulfate in $\text{PM}_{2.5}$ was about 75% of that in TSP. Thus, majority of sulfate was nss sulfate and majority of nss sulfate was in fine particles. The contribution of biogenic sulfur emissions to nss sulfate at the site reported by Arimoto *et al.* (1996) was less than 11%. Thus, most sulfates measured in TSP during the study were from anthropogenic sources.

The mean concentrations of calcium and magnesium, about $0.5 \mu\text{g m}^{-3}$ in TSP and $0.2 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$, were comparable to other measurements at the same site (Carmichael *et al.*, 1996; Kim *et al.*, 1995, 1997a). The mean potassium concentrations in both TSP and $\text{PM}_{2.5}$ were higher than other measurements at the same site. Reflecting the sampling site is at the seashore, the concentrations of sodium and chloride were high in TSP. But after subtracting sea salt fractions, the mean nss chloride concentrations in TSP showed negative concentration, of which the cause is discussed later. The mean concentration of ammonia was $1.45 \mu\text{g m}^{-3}$ while those of nitric acid and hydrochloric acid were both below their LDLs during this study.

The mean concentration of ammonium in TSP was lower than that in $\text{PM}_{2.5}$. The reason for this might be the sampling artifacts associated with sea-salt fraction in aerosol. Sea salt particles are alkaline (the average pH of surface sea water is about 8.2, Horne, 1969) and TSP contains more sea-salt fraction than $\text{PM}_{2.5}$ since most sea salt particles are in coarse mode. When aerosol and sea-salts collide either in the atmosphere or on the filter, two processes might occur: (1) adsorption of acidic gaseous species, such as nitric acid and nitrogen oxides to alkaline aerosol to neutralize aerosol (Prospero and Savoie, 1989) and (2) evaporation of volatile alkaline species, ammonium, to neutralize aerosol (Kim *et al.*, 1995). The degree of evaporation of ammonium in TSP was higher than that in $\text{PM}_{2.5}$ due to more alkaline nature of TSP (Kim *et al.*, 1995; Kim, 1997), and, thus, lower ammonium concentration was observed in TSP than

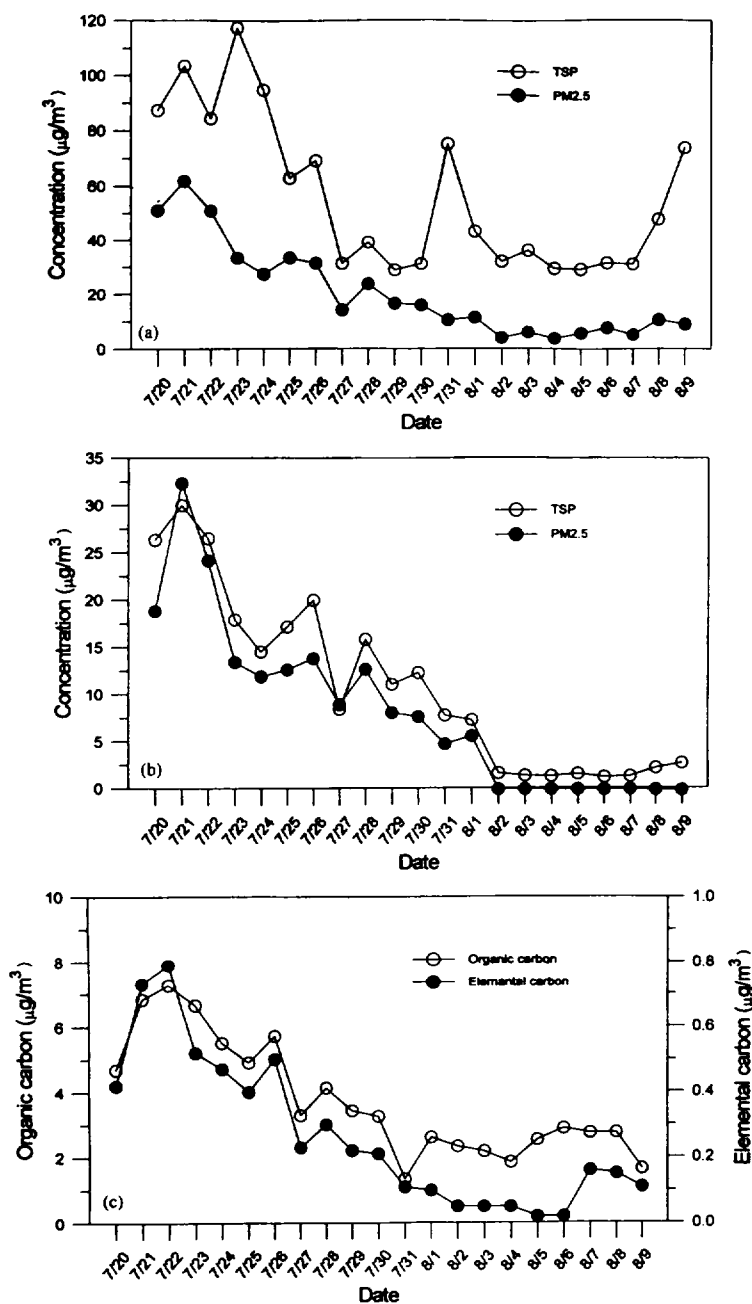


Fig. 2. Trend of daily average concentrations of mass and some of aerosol species concentrations measured during the summer of 1994 at Cheju Island, Korea. (a) Mass concentrations in TSP and PM_{2.5}; (b) Nss sulfate concentrations in TSP and PM_{2.5}; (c) Elemental and organic carbon concentrations in PM_{2.5}.

that in PM_{2.5}. Similar result was observed by Wolff *et al.* (1986). They measured fine and coarse particles at Bermuda and reported that all of the ammonium was in fine particles.

The same kind of sampling artifacts, interactions between acidic and alkaline species in the gas and aerosol phases, also occurred to chloride and nitrate in aerosol. Chloride ions tended to evaporate to form

Table 2. Comparison of water-soluble ions and carbonaceous species concentrations with other measurements

Place	Elemental carbon ($\mu\text{g m}^{-3}$)	Organic carbon ($\mu\text{g m}^{-3}$)	Sulfate ($\mu\text{g m}^{-3}$)	Nitrate ($\mu\text{g m}^{-3}$)	Ammonium ($\mu\text{g m}^{-3}$)	Particle size	References
Cheju Island, Korea (entire period)	0.27 ± 0.05	3.74 ± 0.39	8.40 ± 1.97	0.89 ± 0.24	2.81 ± 0.51	PM ₂	This work
Cheju Island, Korea (20 Jul-1 Aug, 1994)	0.38 ± 0.06	4.58 ± 0.49	13.56 ± 2.16	0.10 ± 0.10	4.24 ± 0.50	PM _{2.5}	This work
Cheju Island, Korea (2-10 Aug, 1994)	0.08 ± 0.02	2.36 ± 0.16	< 1.30	2.16 ± 0.19	0.47 ± 0.07	PM _{2.5}	This work
Nagano, Japan	1.02	1.07	1.22	0.37	0.36	TSP	Hatakeyama (1993)
Okimawa, Japan	1.17	0.78	12.7	1.26	0.83	TSP	Hatakeyama (1993)
Hachijo Island, Japan	0.8	3.1	—	—	—	TSP	Okita <i>et al.</i> , (1986)
San Nicolas Is, USA	0.10	0.81	2.77	0.46	0.68	PM _{2.5}	Chow <i>et al.</i> , (1994)
East China Sea	0.35	—	—	—	—	BC	Parungo <i>et al.</i> , (1994)
Marblemount, USA	0.44	3.06	—	—	—	PM _{2.5}	Malm <i>et al.</i> , (1994)
North Pacific	0.05	$0.2 \sim 0.95$	—	—	—	PM ₂	Lau and Khalil (1993)
Seoul, Korea	7.57	9.97	6.92	1.78	2.63	PM _{2.5}	Moon <i>et al.</i> , (1994)
Beijing, China	2.61	—	—	—	—	BC ^a	Parungo <i>et al.</i> , (1994)

^aBC: Black carbon.

gaseous HCl and thus resulted in negative concentration of nss Cl⁻ (chloride loss) due to the interactions among chloride and other species either on aerosols in ambient air or on the filter media (Harrison and Allen, 1990; Möller, 1990). It is also known that the measured nitrate concentrations in marine environment were generally higher than the actual one due to the interactions between acidic gaseous HNO₃ and NO₂ and alkaline particulate sea salts (Prospero and Savoie, 1989). Thus, concentrations of these ions measured in marine environment, especially in TSP, might contain errors from sampling artifacts.

The mean concentrations of EC in Cheju Island was generally comparable to or lower than the values from other remote areas, even considering the TMO method gives slightly lower values than the TOR method (Chow *et al.*, 1993). BC concentrations reported in Table 2 were measured by aethalometer. As the TMO method, this method can get lower EC values and higher OC values compared to the TOR method (Chow *et al.*, 1993). Contrary to the mean EC concentration, the mean OC concentration at Cheju Island was generally higher than those at several other measurements in remote areas. The mean OC concentration at Cheju Island during the study period was slightly lower than those measured during the SCAQS summer study in Los Angeles Basin, $6.4 \mu\text{g m}^{-3}$ (Chow *et al.*, 1994). Since the mean OC concentration in this study are higher than the sum of EC and OC of other results (Table 2), differences among various analytical methods in EC and OC partition cannot explain the high OC in this study. Recall that the TOR and TMO methods give similar values for the sum of EC and OC. Therefore, it is likely that the high OC and low EC values in this study are not due to the differences in analytical methods.

3.2. Relationship between air pollutant levels

Relationship among some air pollutant concentrations was estimated based on the correlation coefficient matrix and shown in Table 3. Nss sulfate, a typical anthropogenic air pollutant, showed good correlation with mass, EC, OC, nss potassium, and ammonium. However, the relationships between nss sulfate and nss calcium, a typical natural air pollutant, and nss calcium and nss potassium were poor for both TSP and PM_{2.5}. It was shown by Kim *et al.* (1997a) that nss potassium measured at Cheju Island were from both anthropogenic and natural sources. Major anthropogenic sources are biomass burning and industries and major natural sources are dust particles in Northeastern Asia. Poor relationship between nss calcium and nss potassium and good relationship between nss sulfate and nss potassium are consistent with the finding by Kim *et al.* (1997a). Therefore, it is suggested that major fraction of nss potassium measured at Cheju Island were from anthropogenic sources.

Table 3. Correlation coefficient matrix among some species measured at Cheju Island, Korea during summer, 1994

(a) TSP

	nss K ⁺	nss Ca ²⁺	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	Mass
nss SO ₄ ²⁻	0.92 ^a 0.97 ^b	0.16 0.52	-0.74 -0.38	0.98 0.98	0.02 -0.38	0.71 0.63
nss K ⁺	-0.17 ^c	0.79 0.42	-0.64 0.13	0.13 0.93	-0.64 0.13	0.93 0.64
nss Ca ²⁺		0.38 -0.49	-0.29 0.66	0.97 0.07	-0.29 0.66	0.54 -0.31
NO ₃ ⁻			-0.29 -0.37 -0.72	0.50 0.50 0.11	-0.29 -0.37 -0.72	0.85 0.84 0.93
NH ₄ ⁺				-0.12 -0.43 -0.43	0.07 0.01 0.58	-0.17 -0.21 -0.71
Na ⁺					-0.12 -0.43 -0.43	0.66 0.56 0.06
						0.19 0.26 -0.31

(b) PM_{2.5}

	nss K ⁺	nss Ca ²⁺	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	OC	EC	Mass
nss SO ₄ ²⁻	-0.92 ^a 0.90 ^b -0.42 ^c	0.16 0.74 0.11	-0.74 -0.30 -0.73	-0.59 -0.49 0.43	-0.37 0.05 -1.00	0.88 0.81 0.45	0.93 0.90 -0.32	0.97 0.96 -0.74
nss K ⁺		0.28 0.82	-0.52 0.05	-0.52 -0.41	-0.12 0.31	0.77 0.65	0.81 0.71	0.90 0.85
nss Ca ²⁺		-0.20	0.75 0.18 0.08 -0.47	-0.35 -0.22 -0.48 -0.37	0.42 0.36 0.52 -0.11	0.02 0.06 0.37 0.10	-0.30 0.15 0.48 0.73	0.29 0.24 0.79 -0.17
NO ₃ ⁻				0.41 0.09 -0.33	0.60 -0.47 0.73	-0.66 -0.33 -0.48	-0.70 -0.39 -0.28	-0.66 -0.32 0.41
NH ₄ ⁺					-0.44 -0.07 0.19	0.90 0.86 0.49	0.93 0.92 -0.38	0.95 0.94 0.49
Na ⁺						-0.51 -0.30 -0.45	-0.41 -0.19 0.32	-0.29 0.03 0.75
OC							0.95 0.96 0.09	0.89 0.83 0.18
EC								0.93 0.89 0.39

^aValue for the entire period^bValue for the former period^cValue for the latter period

Nss sulfate and nitrate in this study showed negative relationship with high absolute value of correlation coefficients both for TSP and PM_{2.5}. The mean ratio of nss sulfate to nitrate for TSP was about 8.1. Mukai *et al.* (1990) measured PM₁₀ at Oki Island located at the western side of Japanese Islands between 1983 and 1988 and also observed that the nss sulfate to nitrate ratio was about 31 with negative correlation between them. They attributed the negative correlation coefficient between nss sulfate and nitrate to the reactions of collected aerosols with

sulfuric acid particles. Kim *et al.* (1997a) observed similar ratio, 5.6 at Cheju Island with poor relationship between nss sulfate and nitrate during the spring of 1994. On the other hand, Arimoto *et al.* (1996) found that the ratios of nss sulfate to nitrate for the various Asian and Pacific sites varied between 1.7 and 4.8 with high correlation coefficients. They stated several possible reasons for the differences of the ratios in the region. It is not clear at this stage, however, why the ratio values vary widely and relationships differ between several measurements.

3.3. Temporal variations of air pollutant concentration

The whole study period can be divided into two distinctive periods as shown in Fig. 2, a period with high air pollutant concentrations between the start of the measurement until 1 August and a period with low air pollutant concentrations from 2 August till the end of the measurement. The former period corresponded with the first two weather patterns described before, namely, lower wind speed with hot and clear weather and two successive typhoons with little effects on the measurement site. The latter period corresponded to the later two weather patterns, high wind speed with hot and humid weather and a strong typhoon. The means and standard deviations of the mean of air pollutants for each period are also shown in Table 1. Also, in Tables 2 and 3, concentrations of EC and OC for each period and correlation coefficients for each period are shown.

3.3.1. Severe air pollution period. Between 20 July and 1 August, the daily mean nss sulfate concentration in TSP and $PM_{2.5}$ were very high, 16.6 and $13.4 \mu\text{g m}^{-3}$, respectively. These are much higher values than those in other remote areas. Actually, these high values are comparable to the mean sulfate concentration in PM_{3} in Seoul during a heavy smog episode in November 1993, $15.7 \mu\text{g m}^{-3}$ (Baik *et al.*, 1996). The maximum daily nss sulfate concentration of $PM_{2.5}$ during the period was $32.3 \mu\text{g m}^{-3}$ on 21 July. Concentrations of other anthropogenic air pollutants were also high.

The mean concentrations of nss potassium were also higher than that measured at the same site during the spring 1994 (Kim *et al.*, 1997a). During this period, the fraction of the mean concentrations of anthropogenic air pollutants, sulfate, nss potassium, nitrate, and ammonium, to the mass concentration were 0.26 and 0.56 for TSP and $PM_{2.5}$, respectively. For comparison, the average anthropogenic fraction during March, 1994 at the same site for PM_{3} was 0.13 (Kim *et al.*, 1995).

According to the four-day backward trajectory analysis, majority of air masses for this period has moved slowly from either Korean Peninsula or Japanese Islands. For example, the air mass trajectories for 22 July (Fig. 3a), a day with high levels of air pollutant concentrations, clearly showed the influence from Korean Peninsula. Trajectory at 700 hPa, about 3000 m asl, started from northern China four days before its arrival to the Island and passed the Yellow Sea and Korean Peninsula before it arrived at the Island. Trajectory at 850 hPa originated from the Yellow Sea and moved slowly around Korean Peninsula. The surface air mass represented by 1000 hPa started near to Cheju Island and did not move much during the four day period. The air mass trajectories for 24 July (Fig. 3b) showed different patterns. Trajectories represented by 700 and 850 hPa moved from Japanese Island to Cheju Island while that at 1000 hPa moved from the Korean Peninsula.

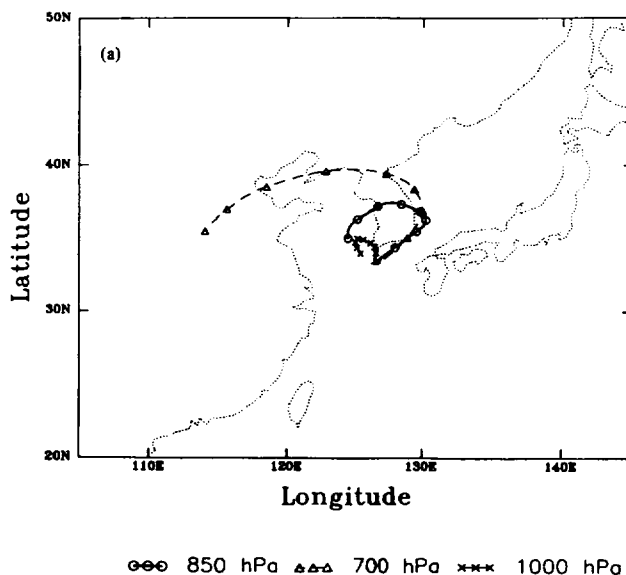
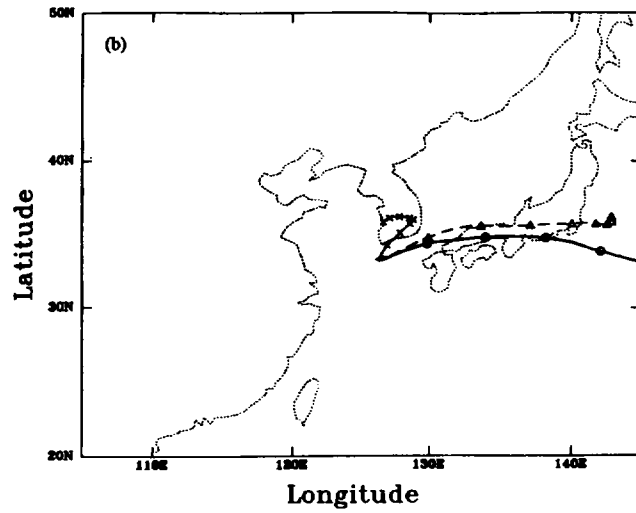
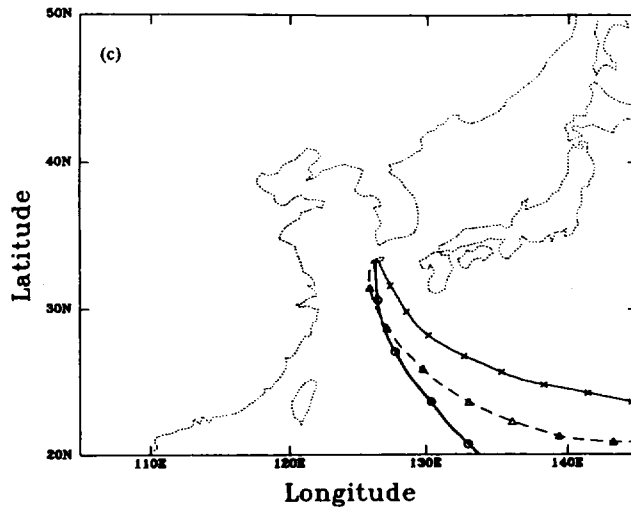


Fig. 3. (Continued opposite) Backward trajectory analysis results for air masses arriving at the sampling site during the summer of 1994 at Cheju Island, Korea. The time interval between two signs was 12 h. (a) 22 July, 1994; (b) 24 July, 1994; (c) 4 August, 1994.



○●○ 850 hPa ▲▲▲ 700 hPa ××× 1000 hPa



○●○ 850 hPa ▲▲▲ 700 hPa ××× 1000 hPa

Fig. 3. (Continued).

This episode with high air pollutant level was caused by the meteorological condition, two anticyclones situated along Korean Peninsula and, thus made the air masses on the area be stagnant. Therefore, primary air pollutants, such as sulfur dioxide and nitrogen oxides, had been converted to secondary air pollutants, sulfate and nitrate, during the air masses from Korea or Japan had been transported to Cheju Island slowly. Thus, the concentrations of mass and other crustal species during this period were similar to

those during other measurements at the site, while those of anthropogenic air pollutants, nss sulfate, nss potassium, and OC, were very high.

3.3.2. *Unpolluted period with marine background air pollutant concentrations.* The concentrations of air pollutants during the latter period were low. The sulfate concentrations in $PM_{2.5}$ were below the LDL, about $1.3 \mu g m^{-3}$ and the mean sulfate concentration in TSP was $2.8 \mu g m^{-3}$, less than 20% of that for the

former period. The mean concentrations of nss potassium and carbonaceous species were also low. The sea-salt species concentrations in this period were higher than those for the former period.

The mean nss sulfate concentration in TSP was comparable to or lower than those reported for various remote areas. The range of sulfate concentrations measured in Bermuda on between 1982 and 1985 was between 2.69 and 3.96 $\mu\text{g m}^{-3}$ (Wolff *et al.*, 1986; Hastie *et al.*, 1988). Also in Oki Island, Japan, the average sulfate concentration in TSP between 1984 and 1988 was 3.59 $\mu\text{g m}^{-3}$. It was also the lowest value measured at the same site. During the spring, 1994, the average nss sulfate in TSP was 8.3 $\mu\text{g m}^{-3}$. At the same site, annual mean concentration of nss sulfate for one year, between 1992 and 1993, was 6.9 $\mu\text{g m}^{-3}$, and that during the summertime was 4.7 $\mu\text{g m}^{-3}$ (Carmichael *et al.*, 1996).

The mean concentration of EC was lower than those in other remote areas. Note, however, that the mean OC concentration during this period, though lower than that for the whole period, is still higher than those at other remote areas shown in Table 2. There are two possible reasons for this high level of OC concentration, even, during the unpolluted period. One possibility is that the OC might be generated from biogenic sources around the Island. The other possibility is that the OC might be generated by photochemical reactions among gaseous hydrocarbons during the transport of air pollutants from outside of the Island. At this stage, it is not clear whether which one is the dominant process. Clearly, more studies are warranted to elucidate this problem.

The concentrations of crustal air pollutants, such as nss calcium and nss magnesium were lower than those measured previously at the same site and comparable to those at other remote areas around the region. The concentrations of ammonium, though anthropogenic air pollutant, were lower than those for the former period because it was forced to evaporate due to the increased level of alkaline sea salts. Thus, ammonia concentration in the gas phase was higher than that during the former period. The same acid-base relationship attracted nitric acid and nitrogen oxides from the gas phase to the aerosol phase and resulted in higher nitrate concentration than that in the former period. Also note that the evaporation loss of chloride, the degree of negative concentration, was decreased due to the same acid-base relationship.

The air masses for the latter period moved fast from the North Pacific Ocean without passing through any land mass during the four-day period. A typical example of air mass trajectories during this period is shown in Fig. 3c on 4 August. All trajectories at 700, 850, and 1000 hPa moved from southeast to the Island. Thus, this level of low anthropogenic air pollutant concentrations during the latter period can be considered as marine background concentration of air pollutants in Northeastern Asia during the summertime. It clearly shows that Cheju Island can be

used as a site for monitoring background concentration in addition to monitoring the long-range transport of air pollutants in the region.

4. CONCLUSIONS

An intensive field study was carried out during the summer of 1994 at Cheju Island, Korea. Concentrations of mass and ions in TSP and $\text{PM}_{2.5}$, elemental and organic carbons in $\text{PM}_{2.5}$, and gaseous species, HNO_3 , NH_3 , and HCl were measured. Backward trajectory analyses were carried out. The main objective of this study was to understand the characteristics of air pollution in Northeastern Asia during summer in which meteorological patterns are different from those in other seasons.

Two distinctive patterns of air pollutant concentration levels were observed. High concentrations of air pollutants between 20 July and 1 August, and low concentrations between 2 and 10 August. During the former period, the mean nss sulfate concentration of $\text{PM}_{2.5}$ was comparable to that in Seoul during a heavy smog episode. Also, concentrations of other ions and carbonaceous species both in TSP and $\text{PM}_{2.5}$ during the former period were high. During the latter period, the average concentration of nss sulfate in TSP was less than 20% of that during the former period. Backward trajectory analysis showed that the air parcels during the former period had moved slowly from Korean Peninsula or Japanese Island while those during the latter period had moved fast from the North Pacific. Also, the air pollutant concentration level during the latter period can be considered as a marine background level in the Northeastern Asia region during the summertime.

Even considering differences in the analytical methods used in different studies, the concentrations of EC during the both periods were comparable to or lower than those at other remote areas in the world. The concentrations of OC, however, were higher than those at other remote areas for the entire study period. This might be due to the biogenic generation of organic aerosol around the Island or/and the generation of secondary organic carbon via photochemical reactions during the transport of gaseous organic species. Further studies are needed to understand mechanisms of high organic carbon concentrations.

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