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SEASONAL VARIATION IN ATMOSPHERIC AEROSOLS CONCENTRATION COVERING NORTHERN KYUSHU, JAPAN AND SEOUL, KOREA

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Abstract—Atmospheric aerosols were collected from October 1990 to February 1992 in northern Kyushu (Tsushima and Ogori), Japan and Seoul, Korea, simultaneously using identical sampling system and chemical analysis methods. Observed data were analyzed with meteorological data to clarify the seasonal variations in aerosol concentration and composition. Dominant ion components of aerosol were SO_4^{2-} in anion and NH_4^+ in cation. The concentrations of ion components were higher in winter than those in summer. Equivalent concentration ratio of particulate nitrate and sulfate (NO_3^-/SO_4^{2-}) showed high value in Ogori having a peak in winter season. Equivalent concentration ratio of Ca^{2+} and sulfate (Ca^{2+}/SO_4^{2-}) is highest in Seoul and shows no seasonal variation. On the contrary, Tsushima and Ogori showed low value in summer season. In summer, this area is affected by the atmospheric high-pressure system which developed at the southern Kyushu sea area and southerly monsoon wind predominate. As the result of this, supply of Ca^{2+} from soil should be diminished in summer. Equivalent concentration ratio of particulate Cl^- and Na^+ (Cl^-/Na^+) in August was half compared with the ratio observed in February. Episode analysis of June 1991 and February 1992 indicated the transportation of pollutants from the outside of Japan. Air masses from the Chinese continent have been concluded to bring the greatest amount of anthropogenic pollutants to Korea and Japan.

Key word index: Atmospheric aerosol, sulfate, nitrate, ammonium, equivalent concentration ratio of aerosols, seasonal variations in aerosol concentration.

INTRODUCTION

Air pollutants such as sulfur dioxide and nitrogen oxides are transformed to the aerosols and removed through the dry- and wet-deposition processes from the atmosphere. The lifetime of aerosols are longer than reactive gaseous pollutants, and it will be important to know the role and weight of background aerosol to clarify the urban aerosol problem. Gotaas (1982) analyzed long-range transport of sulfur and the rate of transformation to sulfate using aircraft measurement. Air trajectory indicated that the polluted air mass observed aloft over Oslofjord (Norway) was transported from England. Estimated transformation rate was $2 \times 10^{-6}\ s^{-1}$. Wakamatsu *et al.* (1990) estimated the rate of transformation to sulfate using volcanic plume measurement from Sakurajima (Japan) and found $3.8 \times 10^{-6}\ s^{-1}$. As the results of rapid increase in fossil fuel consumption in Asian country long-range transport of air pollution has become a serious environmental issue. Mukai *et al.* (1990) measured chemical composition in aerosols collected on the island located in the Sea of Japan and found long-range transportation of aerosols from the mainland of Japan in summer and from Asian continent in water. Seasonal variations in aerosol concentration and composition are important factors to understand the dynamic behavior of aerosols in the atmosphere. Composition and concentrations of aerosol components will be different in space, time and season due to the emission intensity, emission type, chemical reaction and meteorology. In this study, atmospheric aerosols were collected simultaneously covering Japan and Korea using three identical sampling systems. Observed data were analyzed with meteorological data to clarify the seasonal and areal variations in atmospheric aerosol concentration and composition.

EXPERIMENTAL

Aerosols have been collected at three locations in Japan and Korea. As shown in Fig. 1, Seoul and Ogori sites are

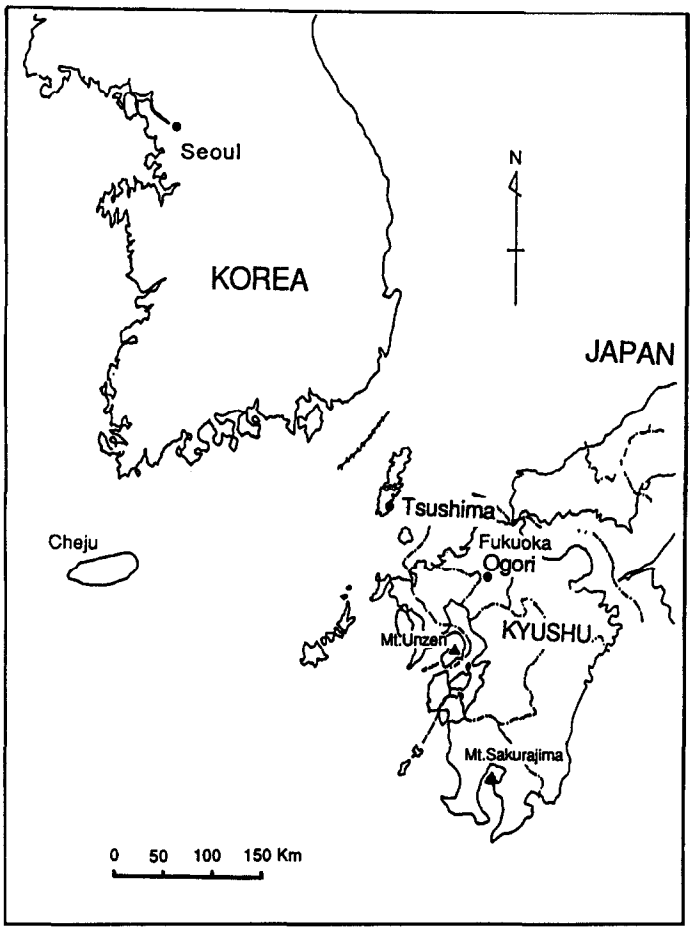

Fig. 1. Sampling site.

located in the inland, while Tsushima in the isolated island. Sampling site in Seoul is located in the NW part of Seoul city. The elevation at the sampling site is 40 m from sea level and sampler was located at the house top, 10 m from the ground. Two heavy roads having four traffic lanes are located at 30 m south and 100 m west from the site. Ogori city is a small town in the suburbs of Fukuoka. The population of this city is 47,000 and 45.5 km^2 in area. The major production in agricultural products and no significant industry exists around the sampling site. The elevation is 20 m and sampler was located at 2.5 m from the ground. Tsushima island is located on Japan and Korea border sea area. The population of this island is 46,000 and 708.25 km^2 in area. The sampling point is located in a remote area and no residence within 2 km around the site and no large pollution source exist. The elevation of the site is 380 m above sea level and sampler was located at 3 m from the surface.

Aerosol samples at three stations were basically collected in the same period every two months from August 1990 to February 1992 by using Model 195 automatic tape air sampler (Kimoto Electric Co. Ltd). Sampling period is one week for a month. The sampling period at Tsushima site was from 12th to 26th of the month which was also the sampling week at Seoul and Ogori. Aerosols were collected during 4 or 8 h successively on rolled polytetrafluoroethylene (PTFE) filters (size 100 mm × 10 m, Type AF-07P, Sumi-tomo Electric Co. Ltd.). Sampling rate was approximately 167 $\ell\,min^{-1}$. The water-soluble particulate components for anion (SO_4^{2-}, NO_3^-, Cl^-) were analyzed by ion chromatography and cation (Ca^{2+}, Na^+, K^+, Mg^{2+}) were analyzed by atomic absorption spectrometer, and NH_4^+ was analyzed by Indophenol method. Detection limits are 0.01 $\mu g\,m^{-3}$ for NH_4^+ and Mg^{2+}, 0.05 $\mu g\,m^{-3}$ for SO_4^{2-}, NO_3^-, 0.06 $\mu g\,m^{-3}$ for Ca^{2+}, 0.08 $\mu g\,m^{-3}$ for Na^+, K^+, 0.12 $\mu g\,m^{-3}$ for Cl^-, respectively.

RESULTS AND DISCUSSION

Seasonal variation of the aerosols

During August 1990 to February 1992, nine series of observation were conducted at three sites in Japan and Korea. The average concentrations of aerosol in the same sampling period, about one week for the month, at the three monitoring sites are summarized in Table 1. In August 1990, sampling was conducted only at Seoul site. In October 1990 and 1991, sampling at Tsushima site was not conducted.

Average particulate anion concentrations during the whole observed period were 13.4 $\mu g\,m^{-3}$, 6.3 $\mu g\,m^{-3}$ and 6.4 $\mu g\,m^{-3}$, and particulate-cation concentrations were 6.4 $\mu g\,m^{-3}$, 2 $\mu g\,m^{-3}$ and 4.6 $\mu g\,m^{-3}$ at Seoul, Tsushima and Ogori, respectively. Dominant aerosol components in anion and cation were sulfate

Table 1. Sampling data at three monitoring sites

Site	Sampling		Sampling period				Sampling interval (h)	Number of sample	Average concentration ($\mu g\,m^{-3}$)							
			Start		End											
	Year	Month	Date	Time	Date	Time			Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+
Seoul	1990	August	10	12	17	8	4	42	0.43	1.48	11.34	3.20	0.96	0.15	0.43	0.45
Seoul	1990	October	15	12	22	8	4	42	0.74	0.95	15.02	4.13	1.15	0.23	0.39	0.76
Ogori	1990	October	15	12	22	8	4	42	0.98	2.68	6.02	2.43	0.52	0.10	0.54	0.53
Seoul	1990	December	10	12	17	8	4	42	0.79	1.67	14.76	4.67	0.61	0.14	0.49	0.77
Tsushima	1990	December	12	18	17	6	4	27	1.63	1.00	5.60	2.08	0.14	0.03	0.64	0.98
Ogori	1990	December	10	12	16	20	4	38	2.50	3.76	6.07	3.66	0.39	0.09	0.45	0.97
Seoul	1991	February	11	12	18	8	4	42	3.06	2.93	7.08	2.73	0.59	0.20	0.33	1.45
Tsushima	1991	February	12	11	19	7	4	40	1.70	0.74	4.50	1.89	0.06	0.05	0.22	1.40
Ogori	1991	February	12	12	19	8	4	42	2.10	2.44	3.36	1.90	0.25	0.11	0.24	0.95
Seoul	1991	April	15	12	22	8	4	42	1.80	1.73	10.58	3.59	0.94	0.27	0.59	0.89
Tsushima	1991	April	15	9	21	17	8	18	1.21	0.83	5.54	1.53	0.37	0.09	0.08	0.93
Ogori	1991	April	15	12	21	12	4	37	1.95	3.78	6.16	3.21	0.45	0.13	0.42	1.09
Seoul	1991	June	10	12	17	8	4	42	0.50	1.32	10.75	3.56	0.92	0.14	0.40	0.50
Tsushima	1991	June	12	10	17	2	8	15	0.35	0.48	6.16	2.24	0.06	0.02	0.07	0.34
Ogori	1991	June	10	12	17	8	4	42	0.88	1.83	3.67	1.59	0.15	0.09	0.23	0.72
Seoul	1991	August	12	12	19	8	4	42	1.35	1.90	10.18	3.69	1.36	0.14	0.30	0.91
Tsushima	1991	August	12	21	19	5	8	20	0.46	0.42	4.69	1.10	0.01	0.02	0.04	0.62
Ogori	1991	August	12	12	19	8	4	42	0.51	2.06	7.05	2.94	0.26	0.11	0.52	0.79
Seoul	1991	October	14	12	21	8	4	42	2.80	1.68	4.82	1.29	1.72	0.12	0.16	0.96
Ogori	1991	October	14	12	21	8	4	42	4.94	2.92	4.58	3.83	0.39	0.12	0.65	1.04
Seoul	1992	February	13	12	21	6	6	32	4.03	4.10	12.79	4.93	1.80	0.18	0.22	1.04
Tsushima	1992	February	13	8	19	8	8	19	2.44	4.52	14.48	3.50	1.37	0.32	0.47	0.98
Ogori	1992	February	13	12	20	8	4	42	3.16	4.67	6.69	4.25	0.56	0.13	0.58	0.88

and ammonium. Monthly variations of average concentration in sulfate, nitrate, ammonium, calcium and chloride at Seoul, Tsushima and Ogori are shown in Fig. 2a–e. Monthly average particulate-sulfate concentration was highest in Seoul with a sharp fluctuation. In Tsushima and Ogori, particulate-sulfate concentrations were almost similar and concentration levels in each month were almost constant throughout the observational period except in February 1992 (Fig. 2a). Nitrate concentrations at Ogori were much higher than that in Tsushima in every month (Fig. 2b). In Seoul, the monthly variations of sulfate and ammonium concentrations showed the same pattern. The ammonium concentration of Ogori was relatively high (Fig. 2c). Calcium concentration was highest in Seoul and lowest in Tsushima except in February 1992 (Fig. 2d). The variation of chloride concentration showed the same pattern at three sites (Fig. 2e). The seasonal variation of particulate nitrate was observed at three sites: the concentration was lower in summer than that observed in winter. In Tsushima and Ogori, the concentrations of chloride and ammonium were lower in summer. Willison *et al.* (1985) compared seasonal variation in atmospheric aerosol concentration in northern England and found that fine particulate nitrate and chloride concentrations had pronounced wintertime maxima and summertime minima. Sopauskiene and Budvytyte (1994) discussed chemical characteristics of atmospheric aerosol in rural site of Lithuania and found a seasonal variation of the major aerosol components such as sulfate and ammonium having a wintertime maxima.

Relationship between aerosol species

Relationship between monthly average equivalent concentrations of anion and cation in Seoul, Tsushima and Ogori are shown in Fig. 3. In Seoul and Tsushima, anion and cation concentrations were well balanced except in February 1992. From the equivalent concentration relationship between anion and cation, the total equivalent anion concentration was higher than that of cation during February 1992 in Tsushima. On the other hand, in Ogori, cation concentration was higher than anion concentration throughout the observational period.

Equivalent concentration ratio of ammonium and sulfate (NH_4^+/SO_4^{2-}) is shown in Fig. 4. Ammonium concentration is higher in Ogori comparing with that in Seoul and Tsushima. Relationship between ammonium and nitrate + sulfate ($NH_4^+/NO_3^- + SO_4^{2-}$) at Ogori site is also shown in Fig. 4. This shows counter anion for NH_4^+ is SO_4^{2-} in Seoul and Tsushima and $NO_3^- + SO_4^{2-}$ in Ogori.

Seasonal variation of equivalent concentration ratio of aerosol components between October 1990 and February 1992 are shown in Fig. 5a–c. Ratio of nitrate and sulfate (NO_3^-/SO_4^{2-}) showed large value in Ogori having a peak in winter season. Ratios of Ca^{2+} and sulfate (Ca^{2+}/SO_4^{2-}) were highest in Seoul and shows no seasonal variation. On the contrary, Tsushima and Ogori showed low value in summer season. In summer, this area is affected by the atmospheric high-pressure system which developed at the northern Pacific Ocean and southerly seasonal wind predominate. As a result of this, supply of Ca^{2+} from soil should diminish in summer. Ratio of Cl^- and Na^+ (Cl^-/Na^+) in August was half compared with the ratio observed in February due to the Cl^- loss in summer. The main source of Cl^- in the atmosphere is sea salt and the equivalent concentration ratio of Cl^- to Na^+ is approximately 1.18. During the summer observation, this ratio was smaller than one. Kadowaki (1977) showed the Cl^- loss reaction in summer based on the field measurement in Nagoya. Particulate nitrate which is observed in coastal area is formed as a result of following reaction between gaseous and particles from ocean spray:

$$NaCl(particle) + HNO_3(gas) \Rightarrow NaNO_3(particle) + HCl(gas).$$

The particulate sulfate is distributed in fine particles and the particulate nitrate is distributed in coarse particles in summer, and it is estimated that the nitrate exists in sodium nitrate.

Episode analysis of the aerosol concentration

Two high-concentration episodes (June 1991 and February 1992) were observed during this series of observation at Tsushima site. In Tsushima, the aerosol concentration was observed within 4 or 8 h intervals from 12th to 26th of every other month as a rule. The mean and maximum concentrations of each observation month in Tsushima are shown in Table 2. Comparing with the six series of observation in Tsushima during December 1990 and February 1992, the highest average concentrations F^-, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} were detected in February 1992. The highest maximum concentrations of F^-, NO_3^-, SO_4^{2-} and Mg^{2+} were also detected in February 1992. The second highest concentration was detected in June 1991. For example the maximum particulate-sulfate concentration was 38.59 $\mu g\,m^{-3}$ on February 1992 and 36.88 $\mu g\,m^{-3}$ on June 1991.

June 1991 episode. Variations of NH_4^+, SO_4^{2-} and NO_3^- in June 1991 in Tsushima and Ogori are shown in Fig. 6a and b. At Tsushima site, the equivalent concentration peaks of particulate sulfate and particulate ammonium were observed on 14th, 17–19th and 22–23rd of June having the similar value of more than 400 neq m^{-3}. At Ogori site, the equivalent concentration peaks of particulate sulfate and particulate ammonium were observed on 15th, 18–19th and 22–23rd of June. This similar time variation observed at two sites indicates the existence of wide areal air pollution covering the northern Kyushu district. In Tsushima, nitrate concentration was at low level. On the other hand, at Ogori site, particulate ammonium and particulate nitrate showed similar pattern with sulfate and ammonium.

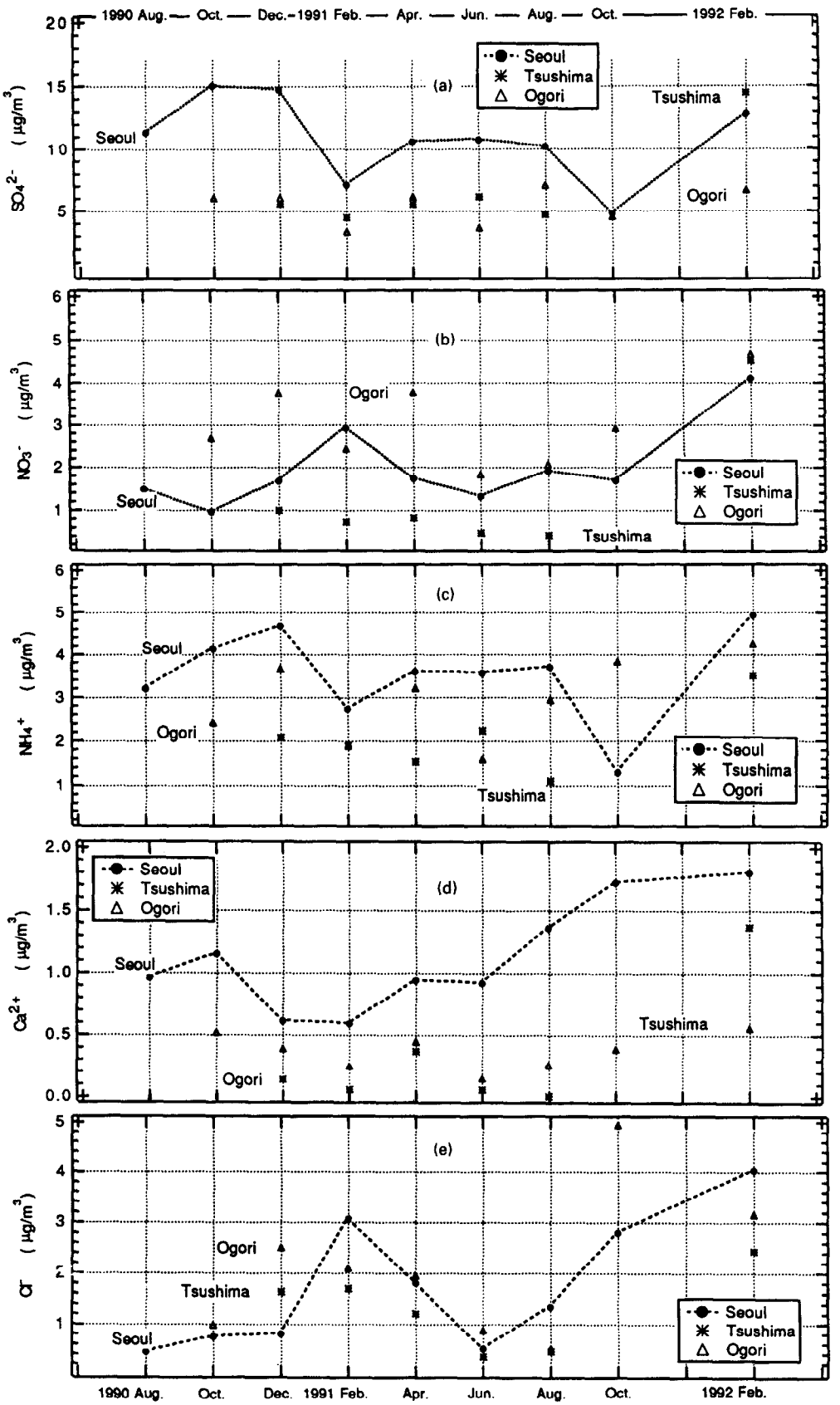

Fig. 2. Seasonal variations of monthly average concentration in (a) sulfate, (b) nitrate, (c) ammonium, (d) calcium and (e) chloride in Seoul, Tsushima and Ogori.

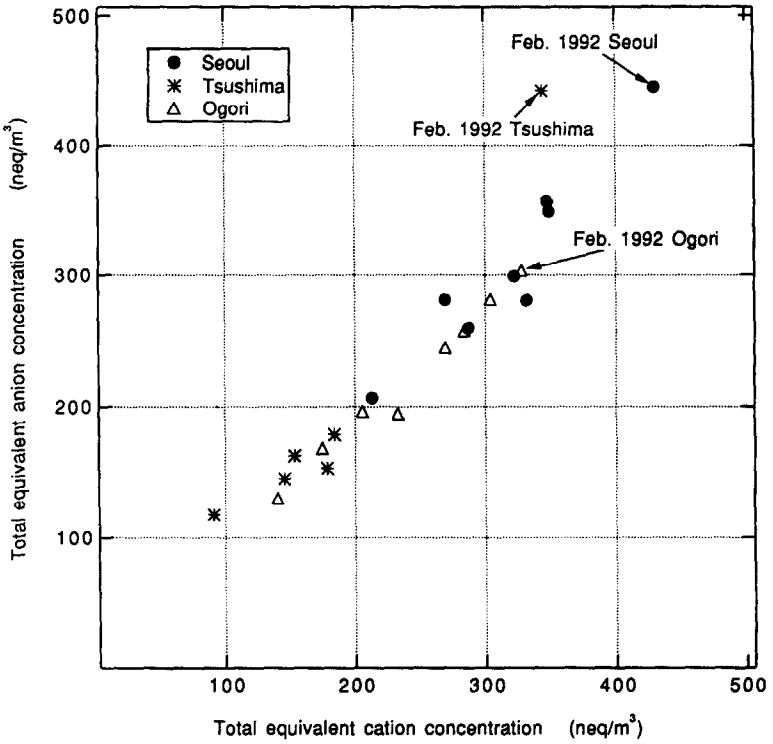

Fig. 3. Relationship between monthly average total equivalent concentrations of anion and cation in Seoul, Tsushima and Ogori.

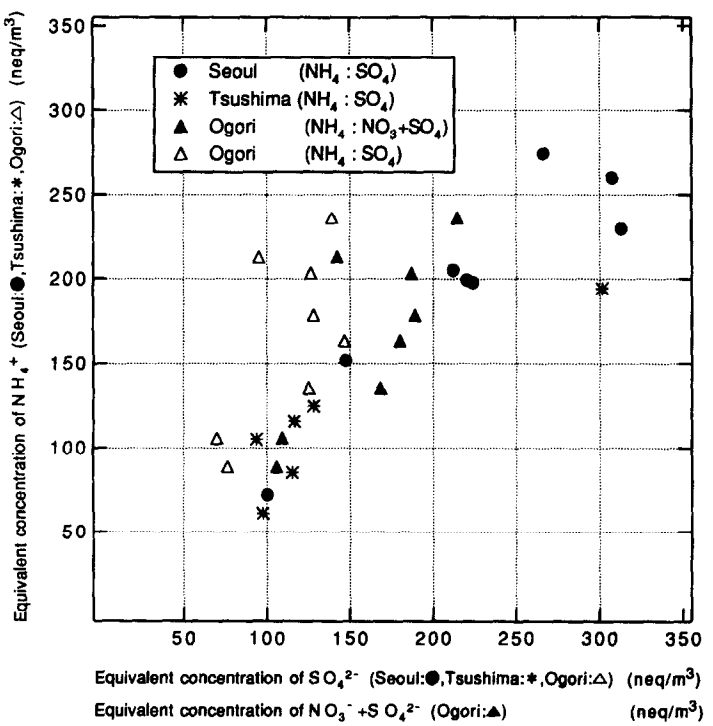

Fig. 4. Monthly average equivalent concentration ratio of ammonium and sulfate (NH_4^+/SO_4^{2-}) in Seoul, Tsushima and Ogori. Relationship between ammonium and nitrate + sulfate ($NH_4^+/NO_3^- + SO_4^{2-}$) in Ogori is also shown in the figure.

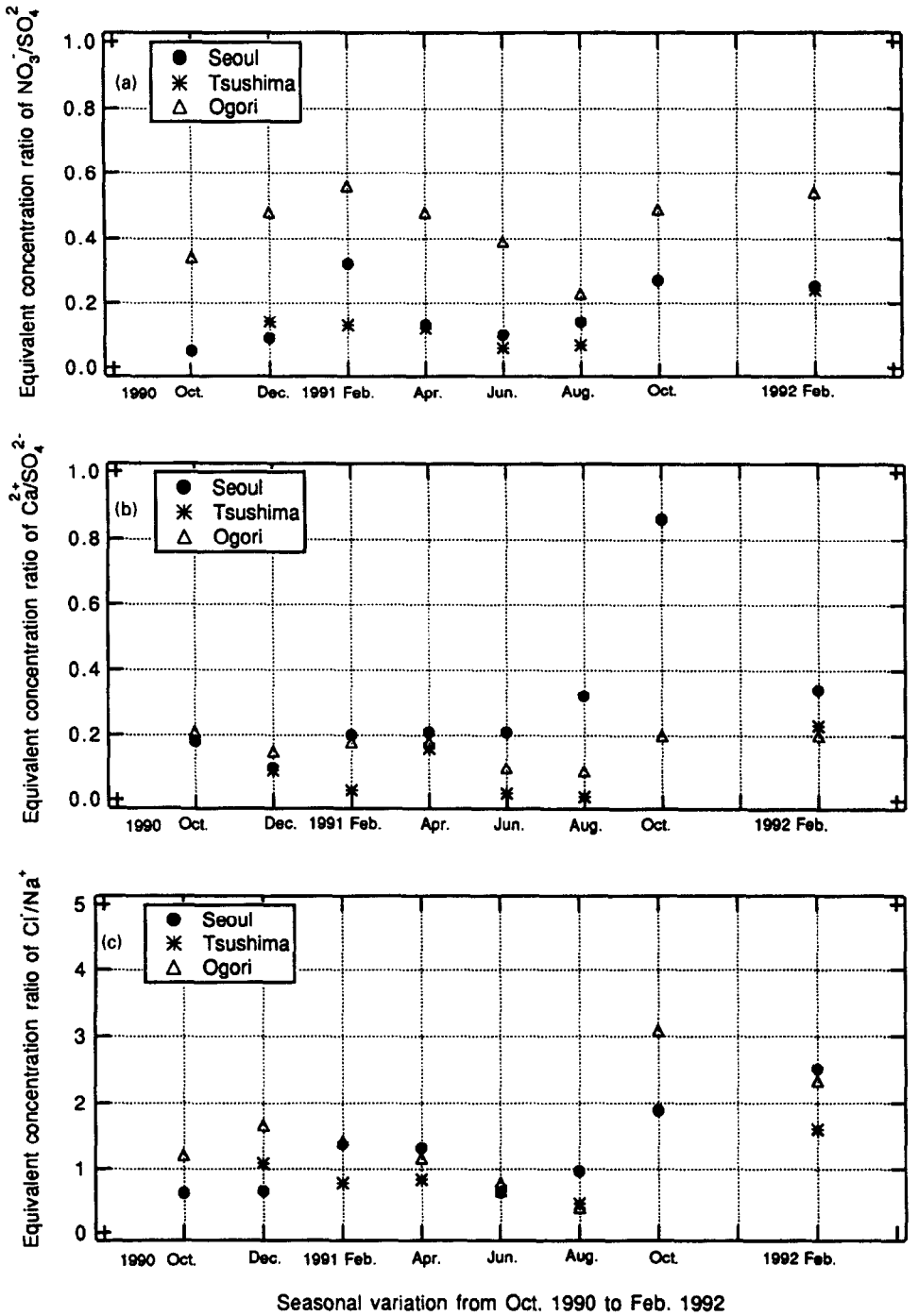

Fig. 5. Seasonal variation of equivalent concentration ratio of aerosol components between October 1990 and February 1992. (a) Ratio of nitrate and sulfate (NO_3^-/SO_4^{2-}). (b) Ratio of Ca^{2+} and sulfate (Ca^{2+}/SO_4^{2-}). (c) Ratio of Cl^- and Na^+ (Cl^-/Na^+).

Tsushima is an isolated island and the sampling site is located on the hill 380 m above sea level. Under these topographical conditions the wind is not affected by configurations of the ground and pollutants such as sulfate which were observed at this site may be remaining intact aloft. On the other hand, Ogori site is located in the inland of Kyushu and northeastern and the western sides are walled by mountains. Under this topography, transported pollutants aloft entrained into the mixed layer and will be diluted. For these reasons, particulate sulfate observed in Ogori is lower than Tsushima. In addition, at Ogori site, it seems to be affected by the relatively higher concentrations of nitric oxide, nitrogen dioxide and ammonium gases near the surface.

Table 2. Aerosol concentrations at Tsushima site

Sampling term		Aerosol concentration ($\mu g\ m^{-3}$)								Sampling time (h)	Number of samples	Total sampling time (h)
		F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+			
12 Dec. 1990–27 Dec. 1990	Mean	0.03	2.00	1.12	6.09	2.16	0.35	0.07	0.61	1.26	4	86	344
	Max.	0.13	7.91	3.94	20.54	5.07	7.68	0.65	1.96	4.94			
12 Feb. 1991–27 Feb. 1991	Mean	0.03	1.54	0.79	4.84	1.99	0.24	0.06	0.22	1.34	4	88	352
	Max.	0.21	4.79	1.80	10.91	4.02	2.08	0.27	0.48	3.21			
12 Apr. 1991–26 Apr. 1991	Mean	0.02	0.68	0.75	5.55	1.66	0.28	0.06	0.07	0.60	8	39	312
	Max.	0.04	4.55	1.98	11.31	3.38	2.23	0.24	0.17	2.97			
12 Jun. 1991–26 Jun. 1991	Mean	0.01	0.27	0.55	11.21	4.13	0.15	0.03	0.12	0.31	8	42	336
	Max.	0.03	1.15	1.69	36.88	13.98	0.96	0.07	0.34	1.20			
12 Aug. 1991–26 Aug. 1991	Mean	0.01	0.51	0.45	4.28	0.86	0.02	0.02	0.04	0.66	8	39	312
	Max.	0.03	1.53	1.32	9.31	2.60	0.07	0.12	0.10	2.26			
4 Feb. 1992–27 Feb. 1992	Mean	0.11	2.05	3.55	14.19	3.35	0.86	0.27	0.39	0.93	8	72	576
	Max.	0.25	5.67	15.97	38.59	8.39	2.83	0.69	1.69	1.69			
Total	Mean	0.04	1.18	1.20	7.69	2.36	0.32	0.09	0.24	0.85		366	2232
	Max.	0.25	7.91	15.97	38.59	13.98	7.68	0.69	1.96	4.94			

February 1992 episode. Variations of NH_4^+, SO_4^{2-} and NO_3^- in February 1992 in Tsushima and Ogori are shown in Fig. 7a and b. In Tsushima and Ogori, the concentration peak of particulate sulfate were observed during the 12th and 14th but sulfate exceeded over ammonium in equivalence in Tsushima. To clarify this, the data of February 1992 were compared with that of February 1991 as shown in Fig. 8a and b. The slope coefficients are 0.96 in Ogori in February 1991, 1.01 in Tsushima in February 1991 and 1.03 in Ogori in February 1992, while the value is 0.57 in Tsushima in February 1992. In February 1991 and 1992, in Ogori, the equivalent ratio of total cation to anion was almost unity, while the ratio was found to decrease in Tsushima during February 1992. It is clear that the total equivalent anion concentration in Tsushima was richer than that of cation in February 1992, and the slope coefficient (ratio of cation to anion) in February 1992 was remarkably small compared with that in February 1991. During the series of this study the main cation components such as Ca^{2+}, Mg^{2+}, K^+, Na^+ and NH_4^+ were entirely analyzed.

Comparing with whole observation, the case in Tsushima in February 1992 is exceptional; that is, the total anion significantly exceeded total cation. Moreover, during this period sulfate concentration was extremely high. Although H^+ concentrations have not directly been measured in this study, considering these observational results we concluded the existence of "acid aerosol" such as sulfuric acid or ammonium hydrogen sulfate in the air which was sampled in Tsushima in February 1992.

The comparison of sulfate and nitrate for February 1991 is shown in Fig. 9a. In the case of 1991, nitrate took a low concentration level in Tsushima while a concentration peak of nitrate was detected in Ogori. The data of February 1992 are shown in Fig. 9b. High concentrations of sulfate and nitrate were detected both in Ogori and Tsushima. The relationship between sulfate and nitrate was found at the two sites during February 1992. Accordingly, the aerosols observed in Tsushima in February originated from anthropogenic pollutants.

The meteorological pattern on 13 February 1992 belongs to the typical winter monsoon season in Japan. The atmospheric high-pressure system located at the western side of Japan and low-pressure system located at the eastern side. Under these atmospheric pressure conditions, northwesterly general wind predominated during the observation. The isentropic backward air trajectory at the level of 850 hPa was calculated using the method of Hayashida *et al.* (1991) and is shown in Fig. 10. Calculated results of 11, 12 and 13 February 1992 indicated that the air mass was transported from the northwesterly direction. From this analysis the high concentration of nitrate and the imbalance of the ionic concentration observed in Tsushima indicate the transportation of anthropogenic pollutants from the west.

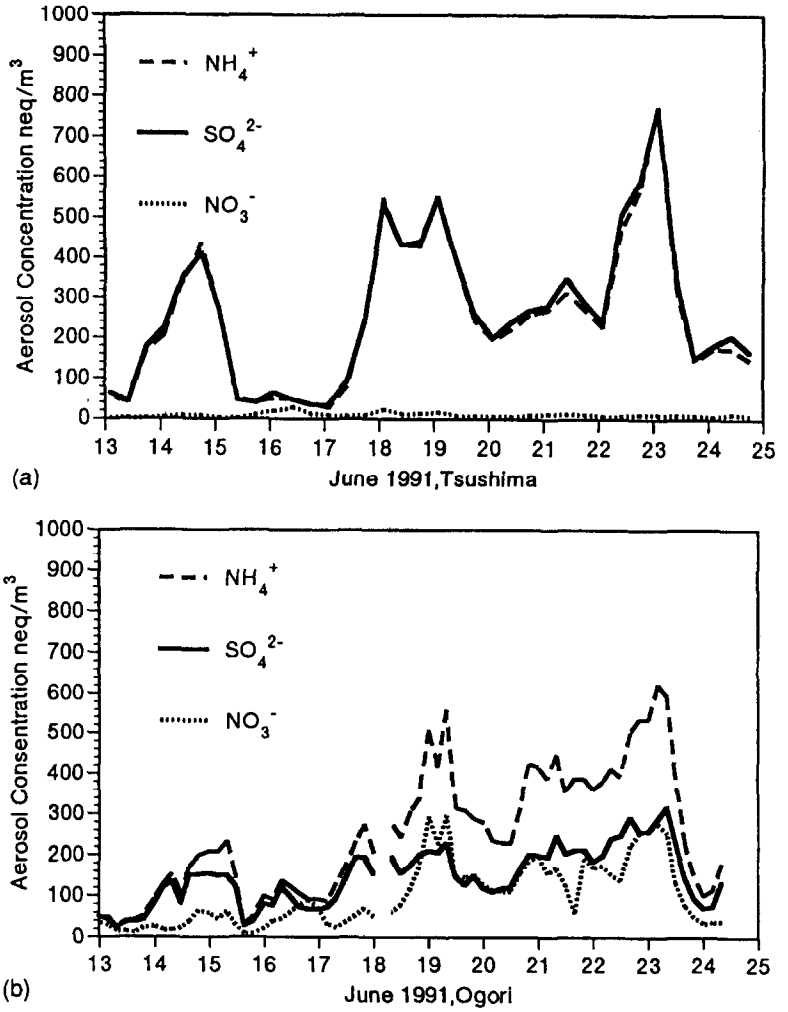

Fig. 6. The diurnal variations of NH_4^+, SO_4^{2-} and NO_3^- on June 1991 in (a) Tsushima and (b) Ogori.

SUMMARY

Aerosol concentrations were observed during October 1990 and February 1992 at Ogori (Fukuoka prefecture, Japan), Tsushima (Nagasaki prefecture, Japan) and Seoul (Korea) in order to analyze the seasonal variations in atmospheric aerosol concentration and composition in northern Kyushu, Japan and Seoul, Korea.

(1) Average aerosol concentrations during the whole observed period were 13.4 $\mu g\,m^{-3}$, 6.3 $\mu g\,m^{-3}$ and 6.4 $\mu g\,m^{-3}$, for anion and 6.4 $\mu g\,m^{-3}$, 2 $\mu g\,m^{-3}$ and 4.6 $\mu g\,m^{-3}$ for cation in Seoul, Tsushima and Ogori, respectively. Major aerosol components in anion and cation were sulfate and ammonium.

(2) Particulate-sulfate concentration was highest in Seoul especially in winter season. In Tsushima and Ogori, concentration levels were almost constant throughout the observational period except in February 1992 in Tsushima. Particulate-nitrate concentration was highest in Ogori and lowest in Tsushima except in February 1992. Particulate-ammonium concentration did not show seasonal variation. Calcium concentration was highest in Seoul and lowest in Tsushima except in February 1992. Seasonal variation of particulate-chloride concentration showed the same pattern at three sites.

(3) Monthly average particulate-ammonium concentration at Ogori was 2.5 times higher in August 1991 and particulate-nitrate concentration was 9.5 times higher in June 1991 compared with the observation at Tsushima. Particulate-nitrate concentrations at Ogori were much higher than that in Tsushima in each month. The monthly average concentrations of particulate sulfate were almost similar in each month. On the other hand, the concentrations of particulate nitrate, chloride and ammonium were lower in summer than that observed in winter.

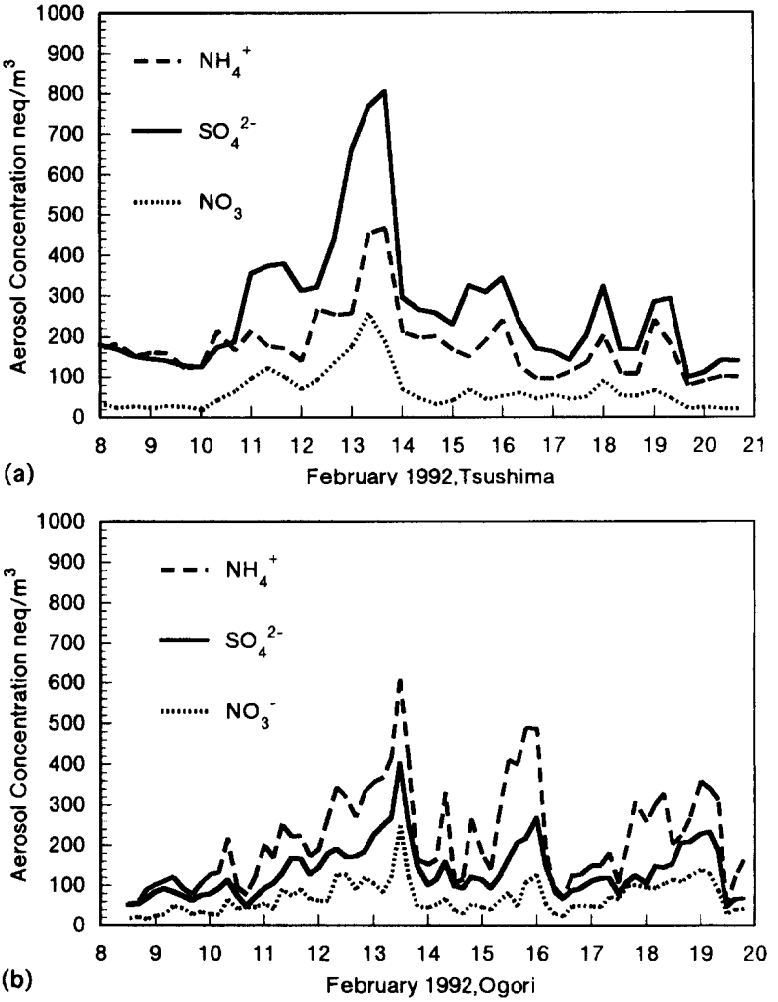

Fig. 7. The diurnal variations of NH_4^+, SO_4^{2-} and NO_3^- on February 1992 in (a) Tsushima and (b) Ogori.

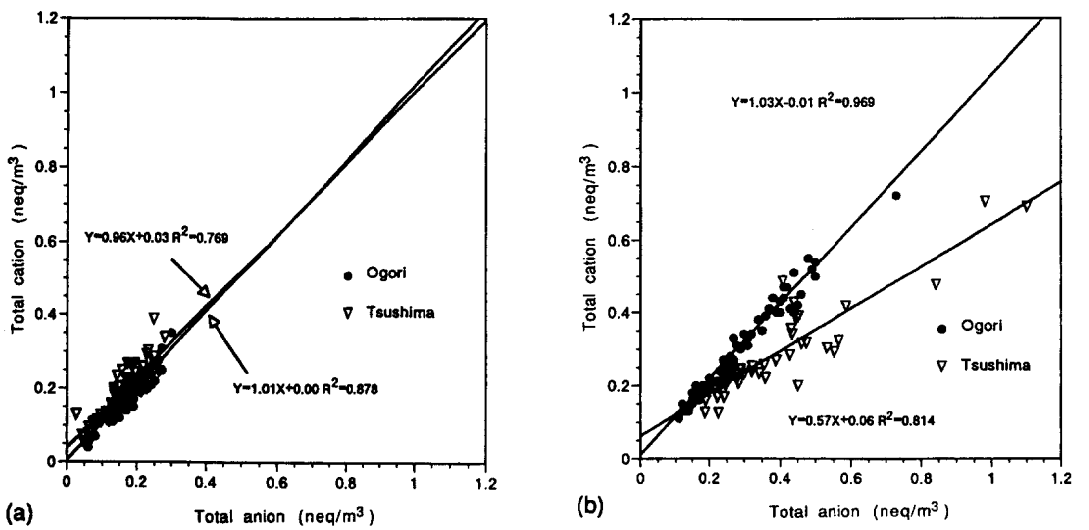

Fig. 8. Relationship between total cation and anion concentrations in Tsushima and Ogori during (a) February 1991 and (b) February 1992.

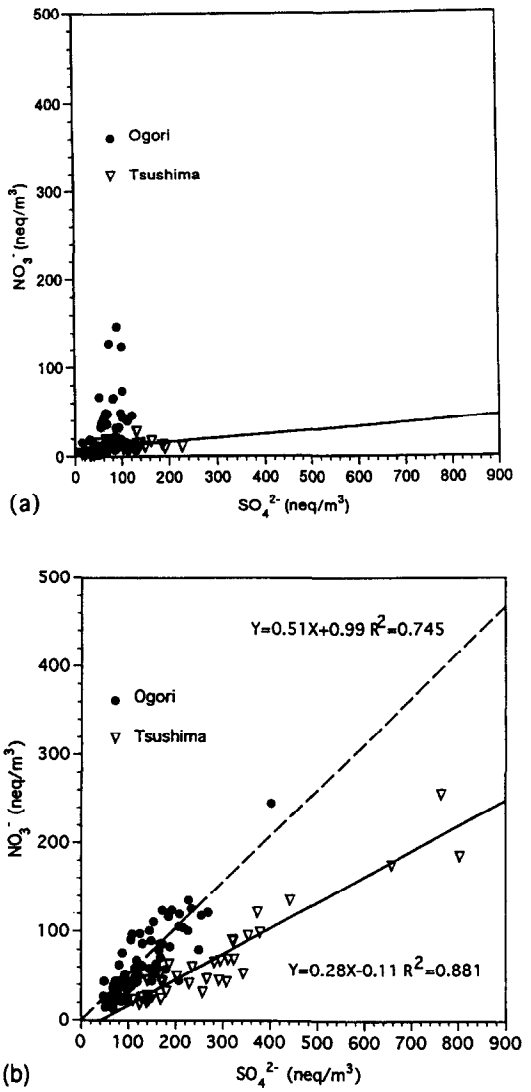

Fig. 9. Relationship between NO_3^- and SO_4^{2-} in Tsushima and Ogori during (a) February 1991 and (b) February 1992.

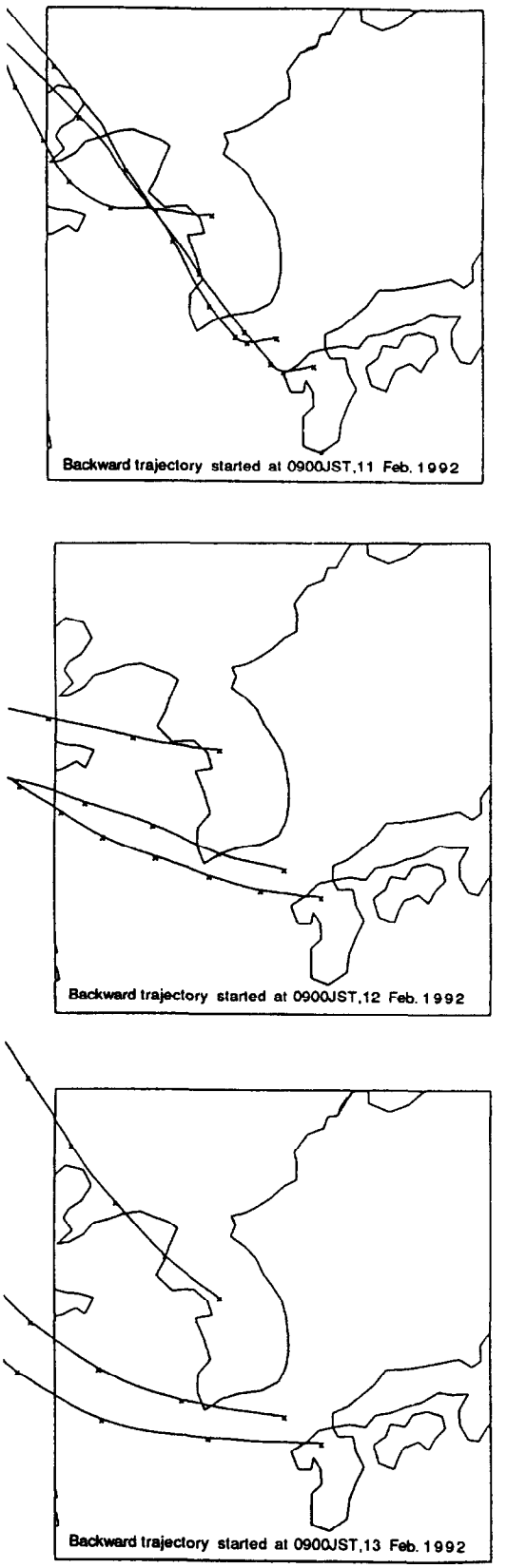

Fig. 10. Calculated results of the isentropic backward trajectory at the level of 850 hPa on 11, 12 and 13 February 1992. Backward trajectory started at 0900JST in Seoul, Tsushima and Ogori, respectively. Mark on the trajectory line (×) shows 6 h interval.

(4) In Seoul and Tsushima, anion and cation concentrations were well balanced except during February 1992. On the other hand, in Ogori, cation concentration was higher than that of anion throughout the observational period. Particulate-ammonium concentration is higher in Ogori comparing with that in Seoul and Tsushima. The counter anion for NH_4^+ is SO_4^{2-} in Seoul and Tsushima and $NO_3^- + SO_4^{2-}$ in Ogori.

(5) Ratio of nitrate and sulfate (NO_3^-/SO_4^{2-}) showed a large value in Ogori having a peak in winter season. Ratio of Ca^{2+} and sulfate (Ca^{2+}/SO_4^{2-}) was highest in Seoul and showed no seasonal variation. On the contrary, Tsushima and Ogori showed low value in summer season. In summer, this area is affected by the atmospheric high-pressure system which developed at the northern Pacific Ocean area and southerly seasonal wind predominate. As a result of

this supply of Ca^{2+} from soil should diminish in summer. Ratio of Cl^- and Na^+ (Cl^-/Na^+) in August was half compared with that observed in February due to the Cl^- loss in summer.

(6) During the June 1991 observation, the concentration peaks of particulate sulfate were measured in northern Kyushu area during 18, 19 and 23 June, and the particulate-ammonium concentration showed the similar pattern with the particulate sulfate at Ogori and Tsushima simultaneously. Particulate nitrate took high concentration level in Ogori while it was low in Tsushima.

(7) High concentration was observed in February 1992 both in Ogori and Tsushima. The peak concentration on particulate sulfate and nitrate at both sites were observed on 13 February 1992. At Tsushima, total equivalent anion exceeded over the total equivalent metallic cation, and this fact indicates the existence of H^+ in the aerosol during the period. The air trajectory analysis indicated that the air mass were transported from the northwestern direction. This high concentration of particulate nitrate and the imbalance of the ionic concentration observed in Tsushima indicated the transportation of anthropogenic pollutants outside Japan.

(8) The monthly average concentrations of particulate sulfate were almost similar in each month, irrespective of the season. On the other hand, the concentrations of particulate nitrate, chloride and ammonium were lower in summer than in winter.

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REFERENCES

Gotaas Y. (1982) Vertical distribution of sulfur in the atmosphere in a case of long-range transport and the rate of transformation to sulfate. *Atmospheric Environment* **16,** 1043–1046.

Hayashida-Amano S., Sasano Y. and Iikura Y. (1991) Volcanic disturbance in the stratospheric aerosol layer over Tsukuba, Japan, observed by the National Institute for Environmental Studies Lidar from 1982 to 1986. *J. geophys. Res.* **96,** 15,469–15,478.

Kadowaki S. (1977) Size distribution and chemical composition of atmospheric particulate nitrate in the Nagoya area. *Atmospheric Environment* **11,** 671–675.

Mukai H., Ambe Y. and Shibata K. (1990) Long-term variation of chemical composition of atmospheric acrosol on the Oki islands in the Sea of Japan. *Atmospheric Environment* **24A,** 1379–1390.

Sopauskiene D. and Budvytyte D. (1994) Chemical characteristics of atmospheric aerosol in rural site of Lithuania. *Atmospheric Environment* **28,** 1291–1296.

Wakamatsu S., Murano K., Uno I. and Ueda H. (1990) Aircraft survey of three-dimensional aerosol distribution. In *Aerosols*, Vol. II, pp. 978–981. Pergamon Press, Oxford.

Willison M. J., Clarke A. G. and Zeki E. M. (1985) Seasonal variation in atmospheric aerosol concentration and composition at urban and rural sites in Northern England. *Atmospheric Environment* **19,** 1081–1089.