

STUDY ON THE FORMATION OF SECONDARY INORGANIC PARTICLES IN HIGH CONCENTRATIONS OF SPM IN KAWASAKI CITY USING TAPE FILTERS

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Water-soluble components in high concentrations of suspended particulate matter (SPM: particles less than 10 μm in size) were analyzed to understand the formation of secondary inorganic particles. This analysis was carried out by using the tape filters of an automatic sampler of SPM at a monitoring station in Kawasaki city. The generation and transportation of secondary inorganic particles in Case I (April 12 and 13, 2006) and Case II (April 18 and 19, 2006) was discussed considering the relationship between the ion concentrations, simultaneously measured gas concentrations, and the results of the backward trajectory analysis of an air parcel. In Case I, it was found that the concentration of NO_3^- increased and the concentration of Cl^- decreased in high concentrations of SPM. From these findings, it was inferred that secondary inorganic particles that were formed by the absorption of gaseous HNO_3 into sea-salt particles in humid air contributed to the increase in the concentrations of SPM. In Case II, it was found that the concentrations of SO_4^{2-} and Ca^{2+} increased in the concentrations of SPM. The results of the backward trajectory analysis of an air parcel showed that the air parcel was transported from the Asian Continent to the Kanto Plain in Japan. Therefore, it was inferred that the Asian dust from the Asian Continent contributed to the high concentrations of SPM. In addition, it was shown that the results from the tape filters and the practical use of relative data were useful in understanding the generation and transportation of secondary inorganic particles.

Key Words : water-soluble components, secondary inorganic particles, SPM, tape filters, asian dust.

1. INTRODUCTION

Although the attainment rate of the environmental standard for suspended particulate matter (SPM: particles less than 10 μm in size) has recently increased in Japan¹⁾, the daily average concentrations of SPM are sometimes observed to be above 100 $\mu\text{g}/\text{m}^3$ according to weather conditions. Yamada et al.²⁾ reported that the decrease in the concentrations of carbon components contributed to the decrease in the concentrations of $\text{PM}_{2.5}$ (particles less than 2.5 μm in size) in Kawasaki city; however, the concentrations of water-soluble components (NO_3^- , SO_4^{2-} , etc.) did not decrease. These water-soluble components constitute the secondary inorganic

particles. Thus, it is important to understand the mechanism of the formation of secondary inorganic particles and the associated chemical reactions.

Several studies³⁾⁻⁵⁾ have sought to understand the characteristics of secondary inorganic particles; in these studies, methods involving the use of impactor-type particle separators for collecting particles and denuders or filter-pack systems for absorbing gaseous pollutants were used. In the case of such methods, the sampling period usually varies from 1 day to 1 week. These sampling periods are sufficient to obtain average concentrations, but they are not sufficient to understand the ever-changing relation between gases and particles according to temperature and humidity. Since field investigations

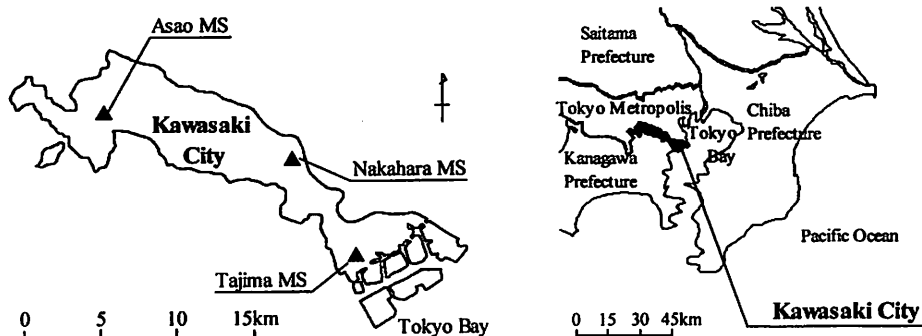


Fig.1 Locations of monitoring stations (MSs).

Table 1 Cases classified by SPM conditions.

	Periods	Concentration of SPM
Case I	April 12-13	Observed above 100 $\mu\text{g}/\text{m}^3/\text{h}$
Case II	April 18-19	Observed above 100 $\mu\text{g}/\text{m}^3/\text{h}$
Case III	April 17	Not observed above 100 $\mu\text{g}/\text{m}^3/\text{h}$

involving a series of short sampling periods are time-consuming and labor-intensive, there is a need to accurately predict when high concentrations of SPM will occur. In Japan, hourly concentrations of SPM are measured by using automatic samplers with tape filters at monitoring stations (MSs). These tape filters can be efficiently used for the chemical analyses of SPM. Nakanishi et al.⁶⁾ reported an analytical method in which the tape filters of the automatic samplers were used at a roadside MS, and they clarified the characteristics of the water-soluble components in $\text{PM}_{2.5}$ in winter. Kasamatsu et al.⁷⁾ reported a strong correlation between the concentrations of water-soluble components (NO_3^- , SO_4^{2-} , and NH_4^+) and the concentrations of SPM in autumn by using the tape filters of automatic samplers of SPM at an ambient MS. More than 1,000 MSs have been set up by local governments in Japan for monitoring air pollutants. Samples of SPM can be easily obtained from the MSs and can be quickly analyzed. Therefore, tape filters are suitable for the chemical analyses of SPM. The gas-particle conversion of secondary inorganic particles was not discussed in the previous works^{6), 7)}. At the MSs, several gaseous pollutants and meteorological elements are measured. The data at these MSs can be used to determine whether secondary inorganic particles are generated near MSs or whether they are

Table 2 Determined pollutants and their respective determination methods at Tajima MS. JIS refers to Japanese Industrial Standards.

	Method	JIS
SPM	β -ray attenuation method	B 7954
NO_2	Colorimetry employing Saltzman reagent	B 7953
SO_2	Conductometric method	B 7952

transported by an air parcel from other places.

In this study, the water-soluble components present in SPM were analyzed by ion chromatography. The samples of SPM were collected using tape filters by the β -ray attenuation method at MSs in Kawasaki, Japan. The generation and transportation of secondary inorganic particles were investigated from the results of the water-soluble components in SPM, the data of gaseous pollutants and meteorological elements obtained at MSs, and the backward trajectory analyses of an air parcel.

2. EXPERIMENTAL

The samples of SPM used in this study were obtained on April 12, 13, and 17–19, 2006. The SPM was observed to be above 100 $\mu\text{g}/\text{m}^3$ on April 13, 18, and 19 without precipitation and was observed to be below 100 $\mu\text{g}/\text{m}^3$ on April 17, throughout Kawasaki city. The samples of SPM were collected by using automatic samplers of SPM (DKK-TOA Corporation, DUB-12); glass fiber (GF) tape filters (DKK-TOA Corporation, 136A303) were used. The samplers had an aerodynamic cut-off diameter of 10

Table 3 Analytical conditions of an ion chromatograph (DX500, Dionex Corporation).

	Anions	Cations
Column	IonPac AS14	IonPac CS12A
Eluate	3.5m mol/L Na ₂ CO ₃ 1.0m mol/L NaHCO ₃	20m mol/L CH ₃ SO ₃ H
Flow	1.2mL/min	1.0mL/min
Suppressor current	25mA	60mA
Injection volume	100μL	100μL

Table 4 Meteorological data from Tajima MS.

	Mean value ± standard deviation		
	Case I	Case II	Case III
Temperature (°C)	16.4±2.2	17.1±2.7	13.9±2.7
Relative humidity (%)	86.9±8.7	58.0±9.9	50.9±20.4
Wind speed (m/s)	1.7±1.4	2.0±0.9	3.0±1.6

μm with cyclone-type particle separators; the sampling flow rate was 20 L/min. SPM was collected at 1-h intervals using the tape filters that had sampling spots (12-mm-diameter circles), and these filters were automatically rolled up at 1-h intervals. The periods were classified as Case I (April 12 and 13), Case II (April 18 and 19), and Case III (April 17), as shown in Table 1. The samples of SPM collected from the MS at Tajima⁸⁾ (139° 42' 42" E, 35° 30' 54" N) were used. The location of the MSs is shown in Fig.1; the Tajima MS is located near a seaside industrial area. Table 2 lists three air pollutants and the methods used for their determination. The tape filters were transported to a laboratory in a cool box and placed in a refrigerator at -30 °C until they were used for the analyses. The water-soluble components present in the SPM collected using the GF tape filters were analyzed by means of an ion chromatograph (Dionex Corporation, DX-500); the analytical conditions are shown in Table 3. Circles with a diameter of 9 mm were cut out from the sampling spots of the GF tape filters every three hours, and the samples were extracted in 10 ml of ultrapure water in a supersonic wave bath for 15 min. The extracted samples were filtered by using disposable filters (Advantec, DISMIC 25HP) and were analyzed for anions (Cl⁻, NO₃⁻, and SO₄²⁻) and cations (Ca²⁺, K⁺, Mg²⁺, Na⁺, and NH₄⁺). The backward trajectories of an air parcel were obtained by using the Meteorological Data

Explorer (METEX) developed by the Center for Global Environmental Research (CGER), National Research Institute for Environmental Studies (CGER-METEX)⁹⁾, which is available online.

3. RESULTS AND DISCUSSION

(1) Weather conditions

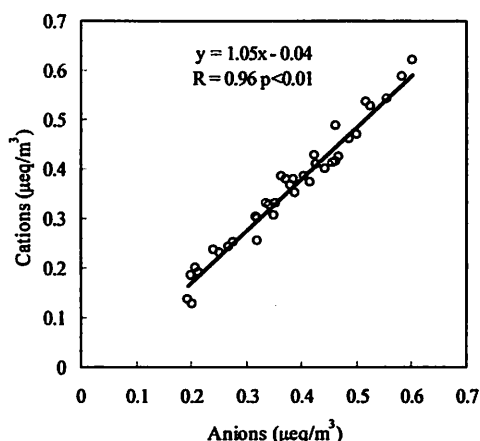
The weather conditions at the Tajima MS are shown in Table 4. In Cases I and II, the average wind speeds were weak and the two average temperatures were close, but the humidity in Case I was characteristically higher than that in Case II. The average temperature and the average humidity in Case III were lower than those in Cases I and II, but the average wind speed in Case III was greater than that in Cases I and II.

(2) Blank filters and ion balance

Blank filters were analyzed in order to study the artifact effects such as the absorption of air pollutants into the surface of GF filters¹⁰⁾. Analyses of the blank filters revealed the presence of Cl⁻, SO₄²⁻, and Na⁺, as shown in Table 5. Yokota et al. have reported the detection of these ions on GF blank filters¹⁰⁾. Since, in this study, the coefficients of variation in the concentration of these ions in the blank filters were 10% or less, the water-soluble components in the samples could be quantified. However, the loss of volatile components and the adhesion of particles to the other side of the sampling spots could not be considered in this study since these effects depended on the condition of rolled-up filters. The ion balance of water-soluble components in the samples is shown in Fig.2. Although the pH values of the distilled samples have not been considered, the anions and cations are well balanced on an equivalent concentration basis, as shown in Fig.2. Because of

Table 5 Ion concentrations and variation of blank filters (n = 5).

Ions	Mean value ($\mu\text{g}/\text{m}^3$)	Coefficient of variation (%)	Detection limit ($\mu\text{g}/\text{m}^3$)	Quantification limit ($\mu\text{g}/\text{m}^3$)
Cl^-	2.26	8.7	0.20	0.65
NO_3^-	N.D.	-	0.02	0.06
SO_4^{2-}	1.94	8.9	0.17	0.56
Na^+	3.44	10.0	0.51	1.69
NH_4^+	N.D.	-	0.06	0.20
K^+	N.D.	-	0.05	0.17
Mg^{2+}	N.D.	-	0.03	0.08
Ca^{2+}	N.D.	-	0.09	0.30

**Fig.2** Relations between the concentrations of cations and those of anions.

this well balance, there seemed to be no sign of secondary organic particles formed by the chemical reaction between carboxylic acid and basic ammonia gas.

(3) Concentrations of water-soluble components in SPM

The concentrations of water-soluble components in SPM in each case are shown in Fig.3, and the mean value and standard deviation are listed in Table 6. In Fig.3, the concentrations of NO_3^- in Case I and SO_4^{2-} in Case II greatly contribute to the high concentrations of SPM. In Table 6, the concentration of NO_3^- in Case I is 2.9 times higher than that of NO_3^- in Case III, and the concentration of SO_4^{2-} in Case II is 1.9 times higher than that in Case III. The hourly concentrations of Cl^- fluctuate each case as shown in

Table 6 Concentrations of ions and SPM in each case.

Ions & SPM	Mean value \pm standard deviation ($\mu\text{g}/\text{m}^3$)		
	Case I	Case II	Case III
Cl^-	2.42 ± 1.24	1.98 ± 0.70	2.19 ± 0.97
NO_3^-	12.71 ± 4.15	5.41 ± 2.29	4.35 ± 2.53
SO_4^{2-}	7.85 ± 2.94	11.45 ± 4.31	6.02 ± 1.60
Na^+	5.67 ± 0.64	4.29 ± 0.65	3.15 ± 0.66
NH_4^+	1.70 ± 0.86	1.45 ± 0.76	0.59 ± 0.44
K^+	0.86 ± 0.41	0.73 ± 0.31	0.32 ± 0.33
Mg^{2+}	0.14 ± 0.03	0.21 ± 0.07	0.09 ± 0.02
Ca^{2+}	0.91 ± 0.27	1.34 ± 0.50	0.47 ± 0.11
SPM	65 ± 35	67 ± 23	20 ± 12

Fig.3; however, the mean values of each case are almost equal in Table 6.

From the values listed in Table 6, we can see that the concentration of Na^+ in Case I is 1.8 times higher than that of Na^+ in Case III, while the concentration of Na^+ in Case II is 1.4 times higher than that in Case III. Since the Tajima MS is located near a seaside area, the concentration of Na^+ was likely to depend on the concentration of sea-salt particles. In Table 6, the concentration of NH_4^+ in Case I is 2.9 times higher than that of NH_4^+ in Case III, while the concentration of NH_4^+ in Case II is 1.9 times higher than that in Case III. The concentration of Ca^{2+} in Case I is 2.5 times higher than that in Case III, while the concentration of Ca^{2+} in Case II is 2.9 times higher than that in Case III. In particular, the concentrations of NH_4^+ and Ca^{2+} increased at the same time in Case II, as shown in Fig.3.

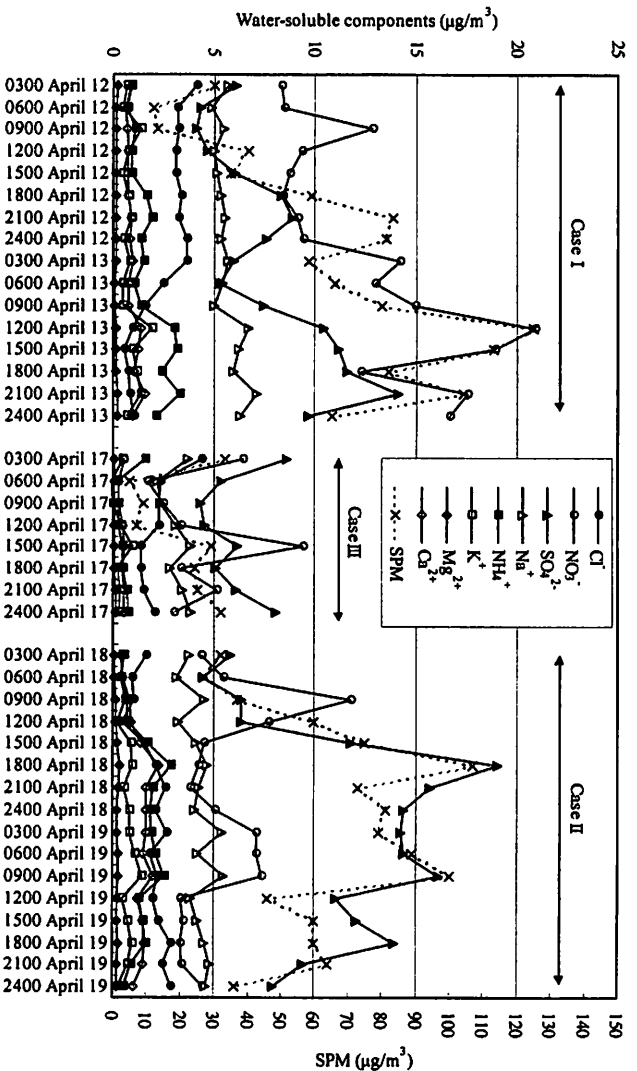


Fig.3 Concentrations of water-soluble components and SPM observed at Tajima MS every three hours.

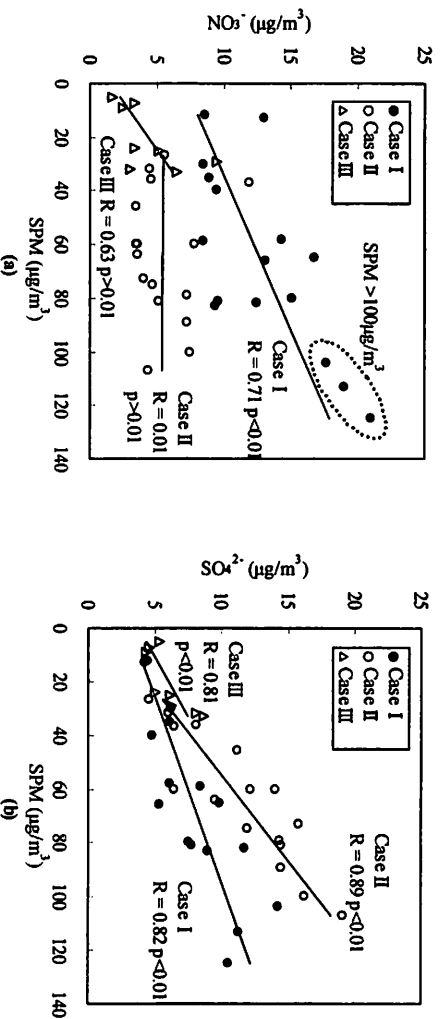


Fig.4 Relations of the concentrations of NO_3^- (a) and SO_4^{2-} (b) to those of SPM.

(4) Relations of the concentrations of NO_3^- and SO_4^{2-} to those of SPM

The relations of the concentrations of NO_3^- and SO_4^{2-} to those of SPM for each case are shown in Fig.4. In Fig.4(a), the concentrations of NO_3^- strongly correlate to those of SPM in Case I rather than in Cases II and III. The concentrations of NO_3^- are particularly high when the SPM concentrations is above $100 \mu\text{g}/\text{m}^3$. In contrast, the concentrations of

SO_4^{2-} correlate to those of SPM for each case in Fig.4(b). Thus, the concentration of SO_4^{2-} is always likely to contribute to that of SPM.

(5) Particle composition determined from water-soluble components

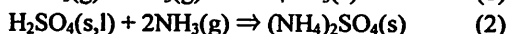
In order to determine counter-ions of NO_3^- and SO_4^{2-} , the correlation coefficients between the concentrations of anions and those of cations were calculated as shown in Table 7. In Case I, the

Table 7 Correlations between anions and cations in each case.

		Correlation coefficients		
Cations		Anions		
		Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Case I	Na ⁺	-0.68(p<0.01)	0.77(p<0.01)	0.83(p<0.01)
	NH ₄ ⁺	-0.81(p<0.01)	0.79(p<0.01)	0.93(p<0.01)
	K ⁺	-0.46(p>0.01)	0.61(p>0.01)	0.52(p>0.01)
	Mg ²⁺	-0.36(p>0.01)	0.35(p>0.01)	0.70(p<0.01)
	Ca ²⁺	-0.70(p<0.01)	0.77(p<0.01)	0.86(p<0.01)
Case II	Na ⁺	0.66(p<0.01)	0.13(p>0.01)	0.57(p>0.01)
	NH ₄ ⁺	0.40(p>0.01)	-0.10(p>0.01)	0.97(p<0.01)
	K ⁺	0.31(p>0.01)	0.08(p>0.01)	0.72(p<0.01)
	Mg ²⁺	0.62(p>0.01)	-0.24(p>0.01)	0.94(p<0.01)
	Ca ²⁺	0.57(p>0.01)	-0.22(p>0.01)	0.95(p<0.01)
Case III	Na ⁺	0.72(p<0.01)	0.73(p<0.01)	0.74(p<0.01)
	NH ₄ ⁺	0.11(p>0.01)	0.43(p>0.01)	0.87(p<0.01)
	K ⁺	-0.06(p>0.01)	0.91(p<0.01)	-0.01(p>0.01)
	Mg ²⁺	-0.11(p>0.01)	0.47(p>0.01)	0.63(p>0.01)
	Ca ²⁺	0.01(p>0.01)	0.66(p<0.01)	0.61(p>0.01)

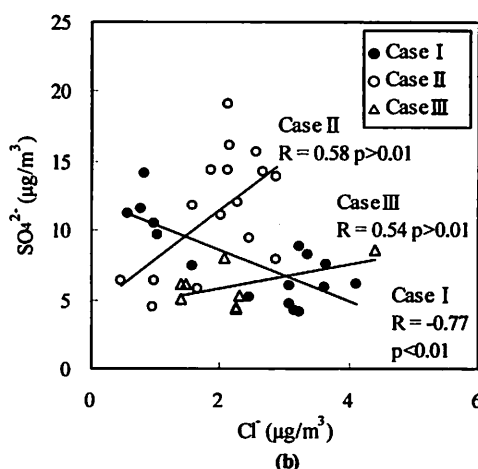
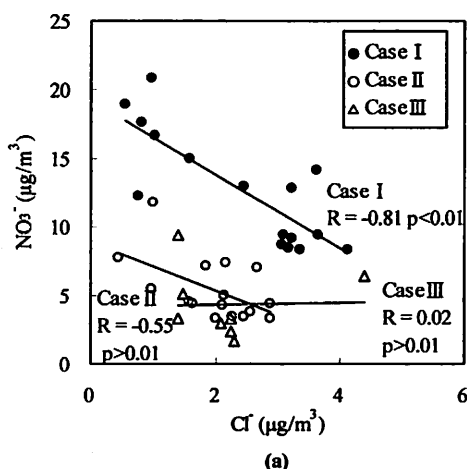
concentrations of NO₃⁻ and SO₄²⁻ strongly correlate to those of Na⁺, NH₄⁺, and Ca²⁺. In Case II, the concentrations of NO₃⁻ have no correlation to any cation, whereas the concentrations of SO₄²⁻ strongly correlate to those of NH₄⁺, Mg²⁺, and Ca²⁺. In Case III, the concentrations of NO₃⁻ correlate to Na⁺, K⁺,

and Ca²⁺, whereas the concentrations of SO₄²⁻ correlate to those of NH₄⁺ and Na⁺. It is well known that gaseous NO₂ and SO₂ are mainly oxidized by OH radicals into gaseous HNO₃ and misty H₂SO₄ mist, respectively, which then form secondary inorganic particles through the reactions given by equations (1) and (2) ^{11), 12)}.



Since the concentrations of NO₃⁻ correlate to those of NH₄⁺ in Case I, the equilibrium of equation (1) seemed to be inclined toward generating a solid state in Case I. In contrast, the concentrations of SO₄²⁻ correlate to those of NH₄⁺ in all cases because equation (2) is a unilateral chemical reaction due to which secondary inorganic particles can be easily formed.

It is generally considered that cations except NH₄⁺ mainly originate from sea-salt particles and mineral-dust particles having sizes between 2.5 and 10 μm ^{11), 12)}. In this study, the concentrations of NO₃⁻ and SO₄²⁻ correlate to the concentration of Na⁺ in Case I, Table 7; the mean concentration of Na⁺ in Case I is 1.8 times higher than that in Case III, Table 6. In Case II, the concentrations of SO₄²⁻ correlate to those of Ca²⁺, as shown in Table 7; the mean concentration of Ca²⁺ in Case II is 2.9 times higher than that in Case III, Table 6. Thus, acid gases are likely to have reacted with sea-salt particles in Case I and with mineral-dust particles in Case II.

**Fig.5** Relations of the concentrations of NO₃⁻ (a) and SO₄²⁻ (b) to those of Cl⁻.

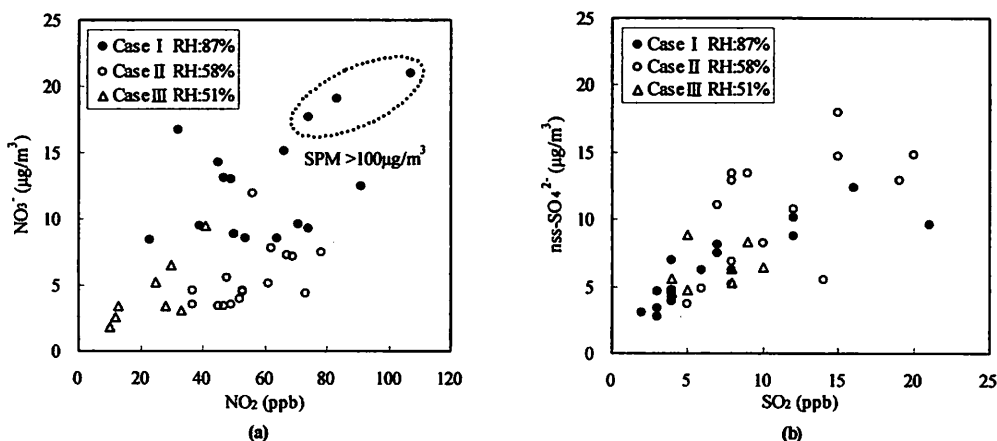


Fig.6 Relations of the concentrations of NO_2 to those of NO_3^- in SPM (a) and relations of the concentrations of SO_2 to those of SO_4^{2-} in SPM (b). RH refers to relative humidity. Other meteorological data are shown in Table 3.

(6) Formation of secondary inorganic particles on sea-salt particles

The formation of secondary inorganic particles occurs not only by gaseous condensation but also by absorption of gases into particles. It is well known that gaseous HNO_3 and H_2SO_4 mist react with NaCl to form NaNO_3 and Na_2SO_4 , respectively. This chemical reaction with sea-salt particles is called the chlorine loss reaction^{11), 12)}. In Table 7, the concentrations of Na^+ correlate to those of Cl^- as positive in Case II and III and as negative in Case I. In Case I, due to the high concentration of SPM, the concentrations of all ions except Cl^- increase, as shown in Fig.3. The concentrations of NO_3^- and SO_4^{2-} correlate to those of Cl^- as negative only in Case I, as shown in Fig.5. Thus, it is inferred that acid gases were absorbed into sea-salt particles in Case I.

(7) Formation of secondary inorganic particles from gaseous pollutants

The relation between the concentration of gaseous NO_2 and that of NO_3^- in particles and the relation between the concentration of gaseous SO_2 and that of nss-SO_4^{2-} (non-sea-salt) in particles are shown in Fig.6. The concentration of nss-SO_4^{2-} is determined by subtracting the concentration of ss-SO_4^{2-} (sea-salt) from the total concentration of SO_4^{2-} , where ss-SO_4^{2-} is 25.1% of Na^+ by weight¹³⁾. The relative humidity (RH), i.e., the difference in weather conditions between Cases I and II is listed in Table 4. It is generally considered that gaseous condensation and

absorption of gases into particles occur easily in humid air containing many minute drops of water to form secondary inorganic particles^{11), 12)}. Karasawa³⁾ carried out field observations and thermodynamic calculations and reported that gaseous HNO_3 forms particles at a lower temperature and high humidity. The concentration of NO_3^- in SPM tends to increase with the concentration of gaseous NO_2 , as shown in Fig.6(a). In Case I, this tendency is remarkable when SPM is observed to be above 100 $\mu\text{g}/\text{m}^3$. The concentrations of NO_3^- in Case I with RH 87% are higher than those of NO_3^- in Cases II and III with RH values of 51% and 58%, respectively. The gaseous NO_2 is oxidized to HNO_3 and forms particles at high humidity under an almost the same temperature. The concentrations of nss-SO_4^{2-} in SPM tend to increase with the concentration of gaseous SO_2 , as shown in Fig.6(b). However, this tendency is independent of humidity. The concentrations of nss-SO_4^{2-} in Case II are partly higher than those of nss-SO_4^{2-} in Case I, but the humidity in Case II is lower than that in Case I. This increasing concentration of SO_4^{2-} is clarified in the next section by discussing the transportation of an air parcel.

(8) Formation of secondary inorganic particles by transportation of an air parcel

Backward trajectories of an air parcel were obtained by using the CGER-METEX⁹⁾. We obtained 96-h trajectories started at heights of 300 m above the Tajima MS in Kawasaki. The trajectories are shown in Fig.7. The concentrations of SPM at the

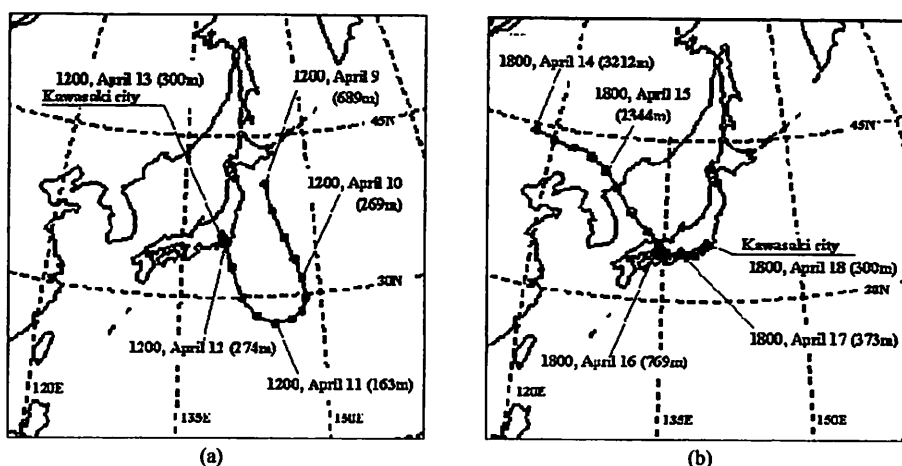


Fig.7 Results of 96-h backward trajectory analyses, started at 1200 (JST: Japan Standard Time) on April 13 and at 1800 (JST) on April 18 at a height of 300 m above Tajima MS in Kawasaki city. The heights of the air parcels at passing routes are shown in brackets.

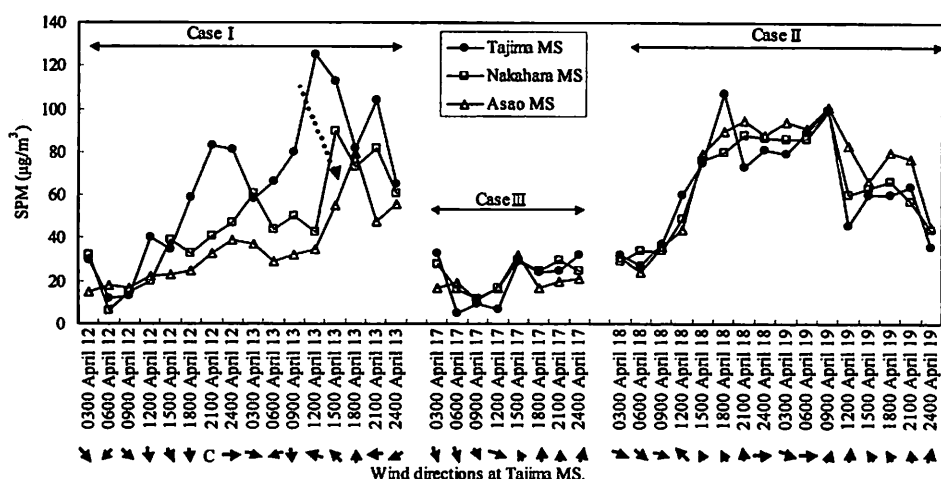


Fig.8 Concentrations of SPM at Tajima, Nakahara, and Asao MSs, taken every three hours. The locations of the MSs are shown in Fig. 1. The arrows below the dates and time indicate the wind directions at Tajima MS, and C indicates calm conditions. In Case I, the dotted arrow indicates estimated air parcel movements from Tajima MS via Nakahara MS to Asao MS.

MSs and the wind directions at the Tajima MS are shown in Fig.8; the locations of the MSs are shown in Fig.1.

In Fig.7(a), the air parcel flowing to Kawasaki is transported over the Pacific Ocean in Case I. The air parcel is likely to have contained sea-salt particles, and this is in agreement with the high concentrations of Na^+ in Case I, Table 6. The air parcel is assumed to have been transported from Tajima MS to Nakahara MS and Asao MS by the south wind, as shown in Fig.8.

From Fig.7(b), the air parcel at a height of 3.2 km

gradually descended toward Japan through the Sea of Japan and the western area of the Japanese islands. The Japan Meteorological Agency reported that Asian dust was transported from the Asian Continent to the Japanese islands except in the northern and northeastern area on April 18 and 19¹⁴⁾. The trajectories show the transportation route of the air parcel containing Asian dust to the Kanto plain, Japan. The concentrations of SPM at three MSs increased simultaneously throughout Kawasaki city in Case II, as shown in Fig.8. The SPM at the Tajima MS must have probably been affected by Asian dust

rather than the air pollutants from the seaside industrial area. It is well known that at high humidity, gaseous SO_2 reacts with CaCO_3 on the surface of Asian dust particles to form CaSO_4 . Kawamura et al.¹⁵⁾ reported that the concentrations of Ca^{2+} and SO_4^{2-} in rain containing Asian dust were higher than those in rain without Asian dust. This report was in agreement with the results of Ca^{2+} and SO_4^{2-} in Case II, Fig.3. Thus, the sorption of SO_2 into Asian dust is likely to have occurred somewhere in the atmosphere over an industrial city and must have led to the increase in the concentrations of SO_4^{2-} in SPM in Case II in Fig.6(b). Through SEM-EDX analyses, Tanabe et al.¹⁶⁾ detected the presence of sulfur element (S) in Asian dust particles collected in Shenyang, an industrial city in China, but they did not detect S in Asian dust particles collected from the Taklimakan Desert and the Loess Plateau. Moreover, through X-ray absorption spectra analyses, they found that S present in Asian dust is mainly in the form of the 6+ valence (SO_4^{2-})¹⁶⁾. Therefore, it has been assumed that the absorption of SO_2 into the Asian dust occurred before the Asian dust particles were transported to Japan. Baek et al.¹⁷⁾ reported that the particles containing a high concentration of SO_4^{2-} and a low concentration of NO_3^- were transported along a long distance because of the long lifetime of SO_4^{2-} .

4. CONCLUSIONS

In order to understand the formation of secondary inorganic particles, we analyzed the water-soluble components in high concentrations of SPM by using the tape filters of an automatic sampler at Tajima MS in Kawasaki city. From the results, it was assumed that gaseous HNO_3 was absorbed into sea-salt particles in humid air to form secondary inorganic particles in Case I (April 12 and 13, 2006) and that the Asian dust was transported from the Asian Continent to the Kanto Plain, Japan in Case II (April 18 and 19, 2006). Further, it was shown that the hourly results of water-soluble components in SPM using the tape filters and the practical use of relative data (gaseous pollutants and meteorological elements) were useful in understanding the generation and transportation of secondary inorganic particles.

Although secondary inorganic particles are one of

the factors that increase the concentration of SPM, the ratios of water-soluble components in SPM are at most 40–50% by weight. It is necessary to consider the concentration of carbon components, the formation of secondary organic particles, etc. Moreover, it should be also considered the artifact effect of rolled-up tape filters to precisely analyze the water-soluble components in particles by using tape filters.

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