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Characteristics of water-soluble components of atmospheric aerosols in Yokohama and Mt. Oyama, Japan from 1990 to 2001

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Abstract

We continuously collected aerosol samples of PM_7 from 1990 to 1997 and of PM_{10-2} and PM_2 from 1998 to 2001 and measured their water-soluble components of pH, conductivity, major ions, dissolved organic carbon (DOC) and total mass (TM) in an urban site, Yokohama ($35°28'N$, $139°38'E$) and the mountainside (680 m asl) of Mt. Oyama ($35°28'N$, $139°46'E$, 1252 m asl), Japan, to contrast the aerosol composition between an urban site and a mountain site. In Yokohama, annual mean TM concentration decreased gradually for over 10 years with the decrease of NH_4^+, Mg^{2+}, Cl^-, and SO_4^{2-} concentrations, and TM concentrations were the highest in winter and the lowest in summer. At Mt. Oyama, there was no significant change in the duration, and TM concentrations were the highest from late spring to early summer, although the seasonal variation was smaller. Equivalent concentration ratio of Cl^- to Na^+ at Mt. Oyama was lower than that in Yokohama, because Cl loss which occurred was larger for the aerosol collected at Mt. Oyama remote from the sea rather than Yokohama. The conversion ratio of sulfur to sulfate was calculated and the ratio was not affected strongly by the variation of O_x concentration at both sites and was high at Mt. Oyama in summer. NH_4^+, NO_3^-, SO_4^{2-}, and DOC concentrations were higher under weak wind velocity than those under strong wind velocity regardless of the wind direction in both the sites.
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1. Introduction

In order to investigate the effect of air pollutants on the natural environment and ecology system, we need to measure not only the wet depositions but also the dry depositions, e.g. gases and aerosols. The dry deposition of aerosols, particularly those containing acidic species such as nitrate and sulfate, causes the acidification of lakes, rivers, and soils. The air pollution of aerosols spreads out over broad regions (Chan et al., 1997; Wakamatsu et al., 1996) because the aerosols remain in the air for several days (Wojcik and Chang, 1997). We have been investigating acid fog at Mt. Oyama in the Tanzawa Mountain on the southwest of the Kanto Plains, where many of the virgin firs are dead. At the mountain, the acid fog events frequently occur and canopies capture the acid fog containing many air pollutants which are carried upward through a mountain slope by valley winds (Igawa et al., 1998, Igawa et al., 2002). We have also measured the air pollution at our university in Yokohama for the comparison of that in Mt. Oyama. Yokohama is a big city abutting on the

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Keihin industrial area, which is one of the most polluted areas in Japan. In the Kanto district, high concentrations of air pollutants are observed in a wide stagnant region extending over the inland part of the plain (Yoshikado and Uosaki, 2000), and the situations occur from late autumn to early winter. Furthermore, high concentrations of sulfur dioxide exceeding the environmental standard value have been observed over broad regions since the volcano in Miyake Island, 150 km south of Yokohama, erupted in the summer of 2000 (Katsuno et al., 2002). The emission rate of sulfur dioxide from volcanic activities is comparable to that from human activities in Japan.

Since February 1990, we have been continuously collecting aerosol samples and measuring their water-soluble components at Yokohama and the mountainside of Mt. Oyama, Japan, to complement the investigation of the various deposition paths of air pollutants. In this paper, we will discuss and contrast the behavior of aerosol in urban and mountain areas by taking into account the characteristics of meteorology and topography.

2. Experiment

2.1. Aerosol sampling sites

Since February 1990, we have been continuously collecting aerosol samples on the roofs of the four (until July 1999) or six-story buildings (since July 1999) in the campus of Kanagawa University in Yokohama (35°28′N, 139°38′E) and at the mountainside (680 m asl) of Mt. Oyama (35°28′N, 139°6′E, 1252 m asl), Japan (Fig. 1). Kanagawa University is located at 26 km south-southwest of Tokyo, about 3 km west of Tokyo Bay, and to the south of Keihin industrial area, which is the largest industrial area in Japan. Mt. Oyama is located at about 50 km west-southwest of Tokyo and abuts on the southwest of the Kanto Plains.

2.2. Aerosol sampling methods

Until 1997 in Yokohama, a low-volume air sampler (Shibata Scientific Technology, Ltd., L-20) equipped with a silica fiber (Advantec, Co., QR-100, 55 mm diameter) was used for the collection of aerosols smaller than 7 μm in particle diameter (PM7) at a pumping rate of 10 l min^{-1}. At Mt. Oyama, another low-volume air sampler (Nippon Kagaku Kogyo, Ltd., model 9023) equipped with a silica fiber (Advantec, Co., QR-100, 55 mm diameter) was used for the collection of PM7 at a pumping rate of 15 l min^{-1}. Since March 1998, in both the sites, NILU filter holders (Tokyo Dylec, Co., model NL20) with cascaded impactors were used to classify aerosols depending on their sizes of 10–2 μm (PM$_{10–2}$)

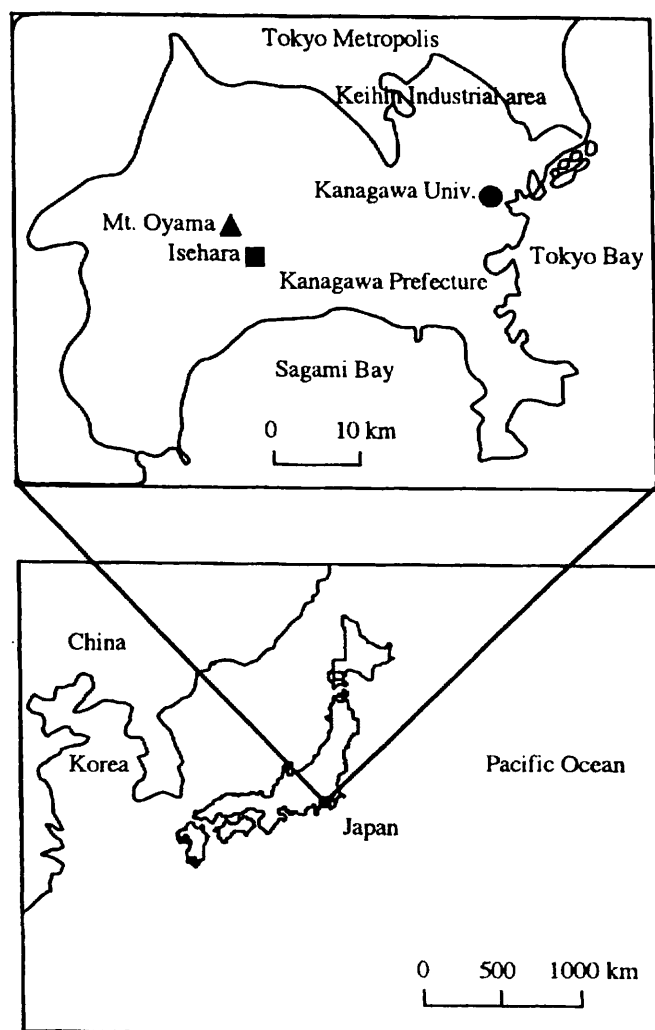Fig. 1. Map of sampling sites.

and smaller than 2 μm (PM$_2$) at a pumping rate of 20 l min^{-1}. Silica fiber filters were equipped in the filter holders (for PM$_{10–2}$, Tokyo Dylec, Co., 2500QAT-UP, 47 mm outside diameter with a pore of 20 mm diameter; for PM$_2$, Advantec, Co., QR-100, 47 mm diameter). In all the sampling periods, the sampling filters were exchanged with new ones every other day in Yokohama and every 7 days at Mt. Oyama. Before and after sampling, all the filters were conditioned for 48 h in a chamber at room temperature at a relative humidity of 50% and then weighed with an electronic balance (detection limit, 10 μg).

2.3. Aerosol analytical methods

The water-soluble components were extracted from the filters into 50 ml ultra pure water in a Teflon beaker by irradiating with ultrasonic waves for 1 h. The water samples were filtered with a 0.45-μm pore-size membrane filter (Advantec, Co., A045A025A). The electric conductivity, pH, and water-soluble ions (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) were measured

using an electric-conductivity meter (Kyoto Electronics, Ltd.. CM-117), a pH meter (Toa Electronics, Ltd., HM-60S), and ion chromatographs for cations except proton (Dionex, Co., DX-100 with a column of Dionex, Co., IonPac CS12) and for anions (Dionex, Co., DX-100 with a column of Dionex, Co., IonPac AS12 or Dionex, Co.. 2000i/sp with a column of Dionex, Co.. IonPac AS4A). The dissolved organic and inorganic carbons were measured with a TOC analyzer (Shimadzu, Co., TOC-5000). The five new filter papers were also extracted, the extracted solution were analyzed, and the average values were used as filter blanks. All the measured concentrations of water-soluble components were corrected with the filter blanks.

2.4. Meteorological conditions and air pollution

The data of wind direction. wind speed, temperature, and relative humidity in Yokohama were provided from Yokohama Local Meteorological Observatory, which was located about 8 km southeast from our sampling site. The oxidant (O_x) concentration data in Yokohama was measured at the office of Kanagawa Ward. located about 1 km east-southeast from our sampling site, which were provided from Environmental Protection Bureau of Yokohama City. The data of total mass concentration of aerosol and SO_2 and O_x concentrations in Isehara was measured at the office of Isehara City situated at the base of Mt. Oyama, which were provided from the Air Preservation Section of Kanagawa Prefecture.

3. Results and discussion

3.1. Soluble components concentrations

Table 1a and b summarize annual mean aerosol concentrations of major ions, DOC, and TM in Yokohama and at the mountainside (680 m asl) of Mt. Oyama from 1990 to 2001, respectively. It should be noted that the collection method of aerosols until 1997 differed from that after 1998. In Yokohama, annual mean TM concentration decreased slowly with the decreases of NH_4^+, Mg^{2+}, Cl^-, and SO_4^{2-} concentrations in the duration from 1990 to 1997, while there was no significant change at Mt. Oyama. Var et al. (2000) reported that the annual average concentrations of some selected crystal elements (Al, Ca, Fe, Mn, Sc, and Ti) and anthropogenic elements (As, Cu. Cr, Ni, Pb, V, and Zn) in the atmosphere in 16 Japanese cities decreased substantially from 1974 to 1996. TM concentration in Yokohama was higher than that at Mt. Oyama every year. This is because Mt. Oyama is relatively remote from pollution sources in urban areas, in comparison with Yokohama. In addition, at Mt. Oyama, the rain

and fog events frequently occurred and canopies captured the aerosols, which are carried upward through a mountain slope by valley winds. At both the sites, the soluble ions accounted for about 30% of TM. The remaining mass was probably due to species such as organic and elemental carbons (Harrison et al., 1997), which were not measured here.

NH_4^+ was the major cation in PM_7, and ammonium salt was the dominant form in the soluble ions of the aerosol collected at both the sites. The correlation coefficient between NH_4^+ and sum of the nss-Cl^-, NO_3^-, and nss-SO_4^{2-} concentrations were extremely high (Yokohama $r = 0.95$, Mt. Oyama $r = 0.96$). The (nss) means (non sea salt) calculated on the basis that all sodium ions originated from the sea salts. In Yokohama, Cl^-, NO_3^-, and SO_4^{2-} were the major anions, while at Mt. Oyama, Cl^- was the minor anion and SO_4^{2-} was the major anion. Satsumabayashi et al. (1998) reported that SO_4^{2-} was the major component at a high altitude in the central mountainous areas in Japan. The mean ratios of the ion concentrations of Yokohama to that of Mt. Oyama between 1990 and 1997 were the highest for Cl^- (7.3) and the lowest in SO_4^{2-} (1.4).

After 1998, aerosols were collected as PM_{10-2} and PM_2. At both the sites, TM of PM_{10-2} were lower than that of PM_2, and the ratio of the soluble ions to TM of PM_2 was a little higher than that of PM_{10-2} (31% of PM_{10-2}, 35% of PM_2 in Yokohama, 28% of PM_{10-2}, 33% of PM_2 at Mt. Oyama). H^+, NH_4^+, K^+, SO_4^{2-}, and DOC, which were mainly derived from human activities and gas- and aqueous-phase reactions, were dominantly distributed in PM_2 all the year around. Na^+, Mg^{2+}, Ca^{2+}, and HCO_3^-, which were transported from natural sources, sea salts and soil dust, were dominantly distributed in PM_{10-2}. Cl^- and NO_3 were distributed in PM_2 in winter and in PM_{10-2} in summer. Similar seasonal trends have also been reported in other papers (Seinfeld and Pandis, 1998; Shimohara et al., 2001).

3.2. Seasonal variation of soluble components concentrations

Fig. 2 shows monthly mean temperature, relative humidity, aerosol concentrations of major ions, DOC, and TM in Yokohama and at the mountainside (680 m asl) of Mt. Oyama from 1990 to 1997. Meteorological conditions at Mt. Oyama was more suitable than those in Yokohama for the formation of aerosols due to low temperature and high relative humidity all the year around; however, each TM concentration in Yokohama was higher than that at Mt. Oyama. In Yokohama, TM concentrations were the highest in winter and lowest in summer, while at Mt. Oyama, TM concentrations were the highest from late spring to early summer with minor seasonal variations. At Mt. Oyama in winter, TM concentrations were not high since the

Table 1

Annual mean aerosol concentrations of major ions, dissolved organic carbon (DOC), and total mass (TM)

Year	Type	H^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	DOC	TM
(a) In Yokohama													
1990	PM_7	0.010	3.4	1.2	0.33	0.17	0.80	2.4	4.7	7.6	NA	NA	69
1991	PM_7	0.011	3.7	0.61	0.35	0.13	0.32	2.3	4.9	5.7	NA	NA	59
1992	PM_7	0.009	3.7	0.60	0.42	0.14	0.51	2.6	4.9	5.9	NA	NA	59
1993	PM_7	0.009	3.0	0.47	0.28	0.092	0.42	1.8	4.6	4.9	NA	NA	51
1994	PM_7	0.008	2.4	0.50	0.28	0.10	0.41	1.4	3.2	4.8	0.11	2.3	51
1995	PM_7	0.008	2.4	0.72	0.38	0.083	0.38	1.6	2.9	4.6	0.064	4.4	41
1996	PM_7	0.008	2.6	0.68	0.37	0.11	0.50	1.6	5.1	3.9	0.057	4.5	50
1997	PM_7	0.008	2.6	0.65	0.27	0.10	0.56	1.6	4.2	4.9	0.024	3.7	47
1998	PM_{10-2}	0.005	0.45	1.1	0.12	0.009	0.056	1.1	2.0	0.90	0.044	0.38	17
1998	PM_2	0.005	2.8	0.28	0.34	0.001	0.023	0.75	4.5	4.0	0.050	0.56	32
1999	PM_{10-2}	0.007	0.56	0.62	0.075	0.036	0.091	1.1	1.9	0.37	NA	NA	14
1999	PM_2	0.011	2.3	0.22	0.23	0.032	0.11	1.9	4.4	1.5	NA	NA	30
2000	PM_{10-2}	0.006	0.29	0.58	0.044	0.045	0.18	0.80	1.5	0.49	0.050	1.2	15
2000	PM_2	0.010	2.3	0.21	0.23	0.004	0.18	1.4	4.3	1.5	0.023	3.3	31
2001	PM_{10-2}	0.001	0.17	0.24	0.089	0.039	0.094	0.24	0.43	0.67	0.062	0.54	7.9
2001	PM_2	0.001	0.80	0.071	0.053	0.003	0.035	0.18	1.1	1.3	0.032	0.86	12
(b) At the mountainside (680 m asl) of Mt. Oyama													
1990	PM_7	0.004	1.5	0.27	0.14	0.070	0.16	0.37	1.6	4.0	NA	NA	24
1991	PM_7	0.003	1.6	0.25	0.14	0.040	0.077	0.27	1.6	3.8	NA	NA	26
1992	PM_7	0.002	1.6	0.20	0.15	0.040	0.088	0.27	1.7	3.7	NA	NA	28
1993	PM_7	0.002	1.2	0.16	0.12	0.041	0.090	0.14	1.5	2.6	NA	NA	20
1994	PM_7	0.003	1.4	0.27	0.15	0.048	0.11	0.15	1.4	3.9	0.018	1.7	22
1995	PM_7	0.004	2.4	0.32	0.21	0.062	0.15	0.61	1.8	5.1	0.022	3.4	32
1996	PM_7	0.002	1.4	0.23	0.15	0.058	0.18	0.15	2.6	2.5	0.009	1.9	25
1997	PM_7	0.002	1.3	0.24	0.14	0.051	0.22	0.15	1.6	3.5	0.009	2.0	23
1998	PM_{10-2}	0.002	0.31	0.24	0.057	0.037	0.17	0.15	1.5	0.85	0.031	0.63	9.9
1998	PM_2	0.004	1.4	0.087	0.11	0.019	0.068	0.12	1.6	3.0	0.019	1.6	15
1999	PM_{10-2}	0.002	0.095	0.20	0.035	0.045	0.12	0.23	0.67	0.30	NA	NA	8.4
1999	PM_2	0.002	1.1	0.059	0.092	0.007	0.047	0.14	1.7	1.6	NA	NA	15
2000	PM_{10-2}	0.002	0.13	0.31	0.021	0.024	0.097	0.22	1.0	0.30	0.015	0.37	9.3
2000	PM_2	0.003	0.81	0.052	0.060	0.009	0.055	0.13	1.7	0.94	0.007	1.4	14
2001	PM_{10-2}	0.001	0.62	0.066	0.031	0.006	0.024	0.13	0.53	1.3	0.023	0.68	7.5
2001	PM_2	0.002	1.3	0.067	0.052	0.011	0.038	0.060	0.20	3.7	0.009	1.8	17

All units are in $\mu g\,m^{-3}$. NA means not analyzed components.

snow event frequently occurs and prevents raising of the soil dust. In most of the components, the monthly variation in Yokohama was more significant than that at Mt. Oyama. In Yokohama, TM and most of the chemical species were the highest in winter and lowest in summer. This is because the north wind prevails in winter and the polluted air of the Kanto Plains is transferred to Yokohama, and the inversion layer frequently occurs and air pollutants are concentrated in inland of the Kanto district in winter.

At Mt. Oyama, NH_4^+ and SO_4^{2-} were the highest in summer due to the formation of H_2SO_4 for the liquid-phase oxidation of gas-phase SO_2, followed by the formation of $(NH_4)_2SO_4$ for rapid reaction with H_2SO_4 and gas-phase NH_3, in high relative humidity. There is no significant source of SO_2 near Mt. Oyama and SO_2 is transferred from abutting the Kanto Plains, where there

are many large factories and plants. The seasonal trends of SO_4^{2-} concentration are also largely affected by photochemical reactions (Husain and Dutkiewicz, 1990).

Table 2 summarizes correlation coefficients (r) between the aerosol concentrations of major anions (Cl^-, NO_3^-, and SO_4^{2-}) and NH_4^+ and the ratio of the former to the latter in Yokohama and at the mountainside (680 m asl) of Mt. Oyama in summer and winter from 1990 to 1997. In Yokohama, in winter, NH_4^+ concentrations correlated well to Cl^- and NO_3^- concentrations. The formations of NH_4Cl and NH_4NO_3 from the reactions of gas-phase NH_3 with HCl and HNO_3 depend strongly on temperature and the decrease of temperature accelerates those formations (Allen et al., 1989; Tanaka et al., 1987). On the other hand, at Mt. Oyama in summer, NH_4^+ concentrations correlated well to SO_4^{2-}
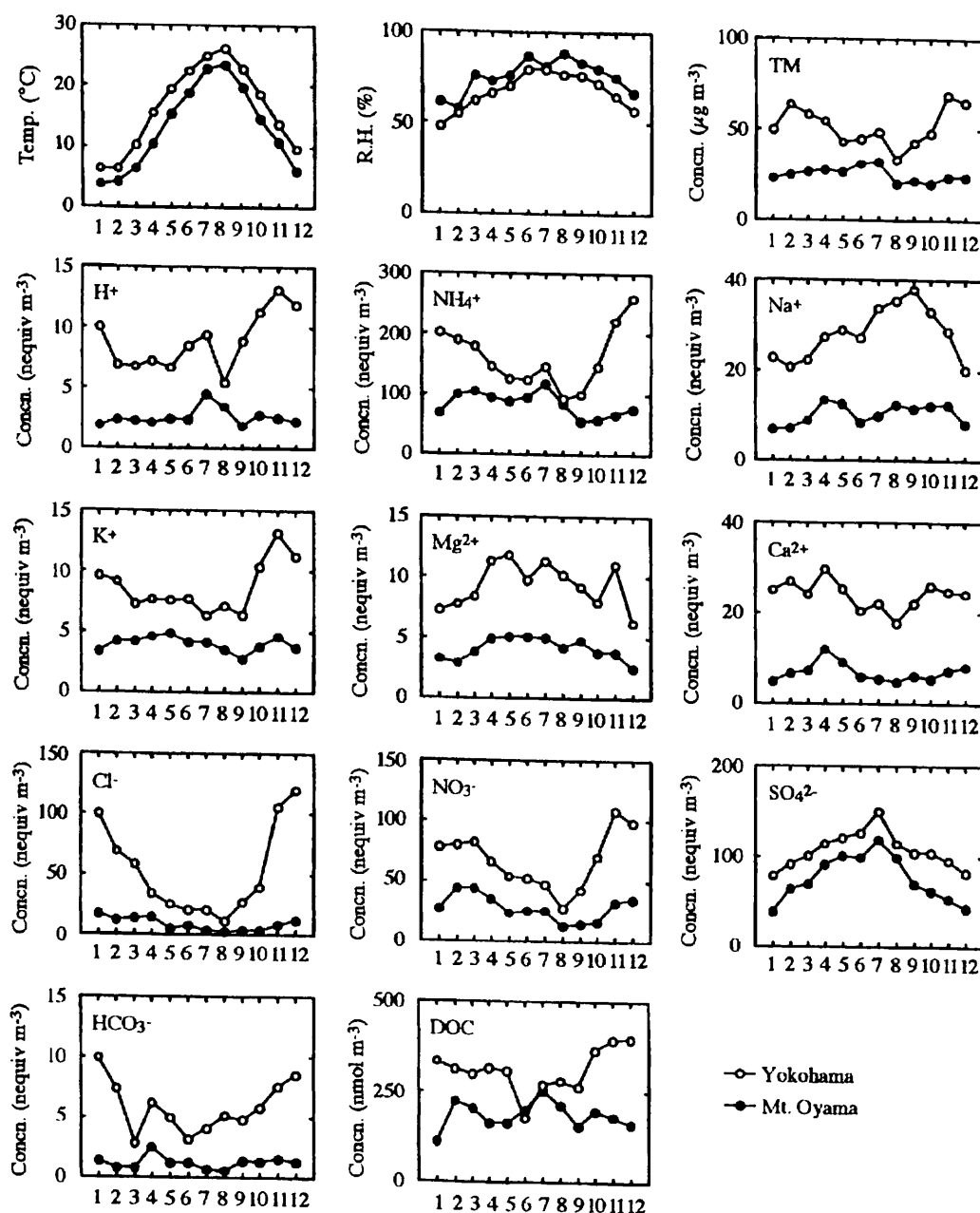
Fig. 2. Monthly mean temperature, relative humidity, aerosol concentrations of major ions, dissolved organic carbon (DOC), and total mass (TM) in Yokohama and at the mountainside (680 masl) of Mt. Oyama from 1990 to 1997.

Table 2

Correlation coefficients (r) and the ratio between the aerosol concentrations ($neq\,m^{-3}$) of major anions (Cl^-, NO_3^-, and SO_4^{2-}) and NH_4^+ in Yokohama and at the mountainside (680 m asl) of Mt. Oyama in summer and winter from 1990 to 1997, respectively

Anion	Yokohama				Mt. Oyama			
	Summer		Winter		Summer		Winter	
	r	Ratio	r	ratio	r	Ratio	r	Ratio
Cl^-	0.00	0.00	0.82	0.38	0.53	0.29	0.18	0.01
NO_3^-	0.18	0.52	0.92	0.38	0.21	0.07	0.72	0.31
SO_4^{2-}	0.84	0.68	0.68	0.20	0.91	0.90	0.79	0.42

concentrations and were nearly equal to SO_4^{2-} concentrations, and hence, $(NH_4)_2SO_4$ was the dominant form of ammonium salt. In winter, the correlation coefficient between NH_4^+ and SO_4^{2-} concentrations was relatively high, and the ratio was higher than for the other two anions. In Yokohama, NH_4Cl and NH_4NO_3 were the dominant forms of ammonium salt; however, NH_4Cl was hardly formed at Mt. Oyama even in winter.

The sea salt is a major component in aerosols near the coast. It was reported that the sum of Na^+ and Cl^- accounted for 60% of the total soluble aerosol mass at the coastal monitoring station in Hong Kong (Cheng et al., 2000). Fig. 3 shows monthly variation of the equivalent concentrations ratio of Cl^- to Na^+ in
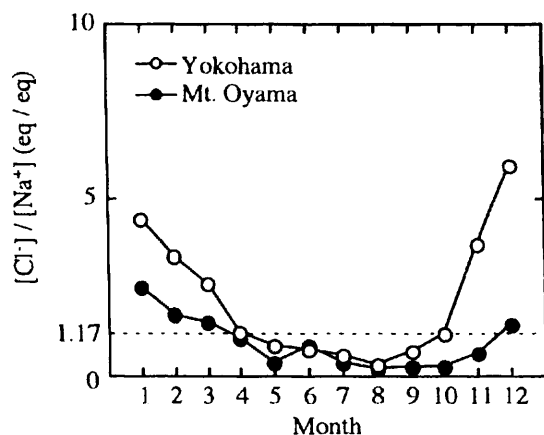
Fig. 3. Monthly variation of the equivalent concentrations ratio of chloride to sodium in Yokohama and at the mountainside (680 m asl) of Mt. Oyama from 1990 to 1997.

Fig. 4. Monthly variation of the conversion ratio of SO_2 to sulfate (F_s) in Yokohama and at the mountainside (680 m asl) of Mt. Oyama from 1990 to 1997 and O_x concentration in Yokohama and Isehara from 1992 to 1997.

Yokohama and at the mountainside (680 m asl) of Mt. Oyama from 1990 to 1997. At both the sites from spring to autumn, the equivalent concentration ratios of Cl^- to Na^+ in the aerosols fell below the ratio in the sea water (1.17), and hence, "Cl loss" occurred. "Cl loss" is explained by the reaction of gas-phase HNO_3 or H_2SO_4 with NaCl in the sea-salt particles. In Yokohama, the reaction of gas-phase HNO_3 may be more predominant than that of H_2SO_4 because, in the coarse particles in summer, the correlation coefficient between Na^+ and NO_3^- concentrations ($r = 0.59$) was higher than that between Na^+ and SO_4^{2-} concentrations ($r = 0.25$). Each equivalent concentration ratio of Cl to Na^+ at Mt. Oyama was lower than that in Yokohama. At Mt. Oyama, the sea salts readily react with the acid gases, and "Cl loss" occurred in the course of the transport because Mt. Oyama is relatively remote from the sea rather than Yokohama (Yokohama, 3 km; Mt. Oyama, 10 km).

Matsuda et al. (1998) reported that the high nss SO_4^{2-} concentration in summer was caused by the oxidation of SO_2 to SO_4^{2-}. To investigate SO_2 oxidation process to SO_4^{2-}, the conversion ratio of sulfur (F_s) was defined as follows:

$$F_s = \text{nss-}SO_4^{2-}[S]/(\text{nss-}SO_2[S] + SO_4^{2-}[S]), \qquad (1)$$

where nss-SO_4^{2-}[S] and SO_2[S] are the non sea salt SO_4^{2-} and gas-phase SO_2 concentration as sulfur, $\mu g\,m^{-3}$, respectively. Fig. 4 shows monthly variation of the conversion ratio of SO_2 to SO_4^{2-} (F_s) in Yokohama and at the mountainside (680 m asl) of Mt. Oyama from 1990 to 1997. At both the sites, the highest F_s were observed in summer and the lowest in winter. Dutkiewicz et al. (2000) reported that 89% of the S was present as SO_2 during October to February compared to 50% during May to August at Whiteface Mountain, New York. The oxidation rate of SO_2 to SO_4^{2-} depends on temperature, relative humidity, radiation, and oxidant (O_x) concen-
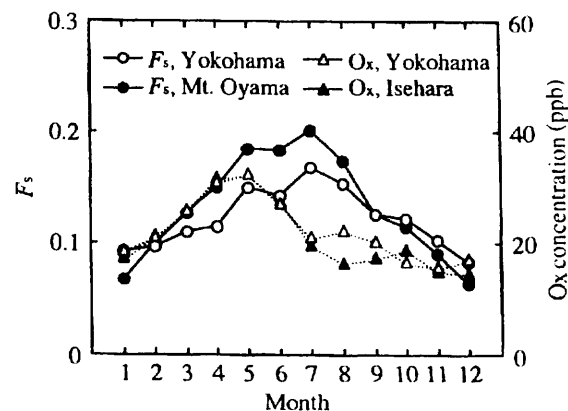
tration. Fig. 4 also shows monthly variation of O_x concentration from 1992 to 1997 in Yokohama and Isehara situated at the base of Mt. Oyama. The monthly variation of F_s did not correspond to that of O_x concentration and O_x concentrations were the highest in spring. Kadowaki (1986) reported that F_s correlated well with the relative humidity when O_x concentrations were more than 20 ppb, suggesting that the droplet-phase reaction was important for SO_2 oxidation to SO_4^{2-}. At both the sites, F_s was not strongly affected by the variation of O_x concentration since O_x concentrations reached about 20 ppb. The F_s at Mt. Oyama was higher than that in Yokohama in summer because the fog events frequently occur at Mt. Oyama in this season. Fog plays a major role in local heterogeneous conversion of SO_2 to H_2SO_4 (Brook et al., 1997). High F_s has been also reported at mountain areas. Satsumabayashi et al. (1999) reported that F_s more than 0.6 were frequently observed in the mountain area (1850 m asl) in autumn. Mori et al. (1999) reported that the F_s ranged from 0.01 to 0.51 and were below 0.35 for 18 out of 22 episodes at Mt. Unzen Nodake (1142 m asl) when high concentrations of SO_2 and SO_4^{2-} were observed for the transported volcano emission.

3.3. Effect of wind

Wind velocity and direction are one of the important factors to determine the aerosol concentrations (Despiau et al., 1996; Wang and Shooter, 2001; Yamamoto et al., 1995). Table 3 shows mean aerosol concentrations of major ions, DOC, and TM at sea and land breezes in Yokohama from 1995 to 1997. The sea and land breezes refer to the breezes from the northeast to southwest and from west-southwest to north-northeast clockwise, respectively. In Table 3, the data are furthermore classified by the average wind velocities (sea breeze, $3.5\,m\,s^{-1}$; land breeze, $3.6\,m\,s^{-1}$), respectively. The sea

Table 3
Mean aerosol concentrations of major ions, dissolved organic carbon (DOC), and total mass (TM) during sea and land winds in Yokohama from 1995 to 1997

WD	WS	H'	NH$_4^+$	Na$^+$	K$^-$	Mg^{2+}	Ca^{2-}	Cl	NO$_3^-$	SO$_4^{2-}$	HCO$_3$	DOC	TM
Sea	<3.5	0.008	2.7	0.72	0.36	0.10	0.50	1.2	4.5	5.2	0.038	4.2	46
Sea	>3.5	0.006	1.9	1.0	0.27	0.17	0.58	1.5	3.3	4.6	0.039	3.6	48
Land	<3.6	0.010	3.5	0.56	0.38	0.079	0.49	2.2	5.3	4.9	0.050	5.0	52
Land	>3.6	0.007	1.8	0.45	0.25	0.062	0.41	1.4	2.8	3.1	0.056	3.2	35

All units are in $\mu g\,m^{-3}$ except WS (m s^{-1}).

and land breezes are predominant in summer and winter, respectively. The TM concentrations at the weak and strong wind velocities were nearly equal to each other in the sea breeze, while in the land breeze the TM concentration during the weak wind was higher than that during the strong wind. In both of the sea and land breezes, NH$_4^+$, NO$_3$, SO$_4^2$, and DOC concentrations during the weak wind were higher than those during the strong wind velocity. These components were mainly derived from secondary particles and from human activities. Although the sea-salt components such as Na$^+$ and Mg^{2+} concentrations during the sea breeze were higher than those during the land breeze, the difference of Cl concentration was indistinct between both the breezes because of the "Cl loss" described in Section 3.2. During the land breeze, only HCO$_3^-$ concentration at the strong wind velocity was higher than that at the weak wind velocity. This is because soil dust and disintegrated rocks were raised by the strong wind.

4. Conclusions

Characteristics of water-soluble components of atmospheric aerosols in an urban site, Yokohama, and a mountain site, the mountainside of Mt. Oyama, were investigated. The points of the aerosol characteristics in common and in contrast between the two sites were summarized as follows. (1) In Yokohama, annual mean total mass (TM) concentration decreased gradually with the decrease of NH$_4^+$, Mg^{2+}, Cl$^-$, and SO$_4^{2-}$ concentrations, however there was no long-term significant trend at Mt. Oyama between 1990 and 1997. (2) In Yokohama, TM concentrations were the highest in winter and the lowest in summer, while at Mt. Oyama, the TM concentrations were the highest from late spring to early summer with minor seasonal variations. (3) In Yokohama, NH$_4$Cl and NH$_4$NO$_3$ were the dominant forms of ammonium salt; however, NH$_4$Cl was hardly formed at Mt. Oyama in winter. (4) At Mt. Oyama, the effect of Cl loss is large because Mt. Oyama is remote from the sea rather than Yokohama. (5) The conversion ratio of sulfur to sulfate was not affected strongly by the

variation of O$_x$ concentration at both sites and was high at Mt. Oyama in summer. (6) At both sites, NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, and dissolved organic carbon concentrations at the weak wind were higher than those during the strong wind velocity. The dominant factors affecting the points in contrast are caused by the difference of the distances from the sampling sites to the pollutant source and sea, and temperature.

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