Characteristics of atmospheric nitrogen and sulfur containing compounds in an inland suburban-forested site in northern Kyushu, western Japan

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ABSTRACT

To evaluate the effects of the regional pollutant emission and long-range transport from East Asia of nitrogen and sulfur pollutants on air quality at an inland suburban-forested site in northern Kyushu, western Japan, nitrogen and sulfur pollutants were characterized from May 2006 to April 2007 using an annular denuder system. The annual mean concentration of HNO_3 (2.16 μg m^{-3}) at the study site was comparable to concentrations reported in urban areas. The HNO_3 concentration had a diurnal variation, being higher in daytime and lower at night. The diurnal variation of wind direction suggests air pollutants emitted from the regional urban area were transported to the study site during the daytime and caused a higher HNO_3 concentration. The HNO_3 concentration was significantly higher in summer and spring than in winter. The annual mean concentrations of SO_2 and nss-SO_4^{2-} (6.52 and 7.70 μg m^{-3}, respectively) were higher than concentrations determined in other urban areas and forested areas near urban areas in Japan and other countries. The SO_2 concentration was significantly higher in winter and spring than in summer. Backward trajectory analysis indicates the long-range transport from East Asia partly contributed to the higher concentrations of SO_2 in winter and spring. In contrast, there were no statistical differences in the nss-SO_4^{2-} concentrations among seasons, which could be explained by increased oxidation of SO_2 to SO_4^{2-} in summer. The value of sulfur conversion ratio (F_s) being higher throughout the year at the study site (52.6%) than values determined in urban sites and there being no diurnal variation of F_s indicates the long-range transport of nss-SO_4^{2-} not only from East Asia but also from other areas including Japan. The equivalent ratio of NH_4^+ and nss-SO_4^{2-} at the study site (0.96 ± 0.22) indicates that acidic sulfate is neutralized by NH_3, existing mainly as $(NH_4)_2SO_4$ in fine particles. On the other hand, NH_4NO_3 had scarcely formed at the study site, unlike the case for urban areas. Ca^{2+} and Na^+ are suggested to be the counter ions of NO_3^- in coarse particles, which is similar to the situation for the sites where the concentration of NH_3 is insufficient for NH_4NO_3 to form.

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1. Introduction

Adverse effects of elevated atmospheric nitrogen and sulfur deposition on forests have been a serious problem over the last few decades (Ågren and Bosatta, 1988; Aber et al., 1989; Galloway, 1995; Driscoll et al., 2003). Atmospheric deposition of nitrogen and sulfur is generally high in urban- and suburban-forested areas, partly due to a higher concentration of atmospheric nitrogen and sulfur compounds (Fenn and Kiefer, 1999; Dambrine et al., 2000; Chiwa et al., 2003a, b; Michopoulos et al., 2004; Aikawa et al., 2006; Chiwa et al., 2008). Therefore, measurement of atmospheric nitrogen and sulfur containing compounds is important in evaluating atmospheric deposition in a forested site.

The atmospheric concentration of air pollutants is controlled not only by regional pollutant emissions but also by the intercontinental long-range transport of air pollutants (Wilkening et al., 2000; Akimoto, 2003). Because Japan has

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been suffering from the long-range transport of air pollutants from East Asia (Mukai et al., 1990; Wakamatsu et al., 1996; Takeda et al., 2000; Shimohara et al., 2001; Uematsu et al., 2002; Matsumoto et al., 2003; Lin et al., 2008), the long-range transport of nitrogen and sulfur air pollutants from that region would be an important contributor to the ambient air quality of nitrogen and sulfur in a Japanese forested area. Although the long-range transport of nitrogen and sulfur air pollutants from East Asia to Japan has been recognized and evaluated at the remote islands around Japan (Mukai et al., 1990; Wakamatsu et al., 1996; Matsumoto et al., 1998; Shimohara et al., 2001; Matsumoto et al., 2003; Takami et al., 2006), only a few studies have been carried out in inland forested areas (Satsumabayashi et al., 1999).

Because many forested areas in Japan are located inland, forested areas, especially inland suburban-forested areas, would be affected by the air pollutants derived from upwind regional urban areas, as well as those from East Asia. Therefore, it is important to evaluate the effects of upwind regional emission and the long-range transport of nitrogen and sulfur pollutants on the ambient air quality at Japanese forested sites. However, little information is available for a downwind inland suburban-forested site with respect to such ambient air quality.

The study site is located 15 km inland of the Fukuoka metropolitan area, Kyushu district (Fig. 1). This site is moderately polluted; a site approximately 2 km east of the study area receives 15 kg N ha^{-1} yr^{-1} and 17 kg S ha^{-1} yr^{-1} via throughfall plus stemflow (Chiwa et al., 2010). It is expected that higher atmospheric deposition of nitrogen and sulfur at the study site is caused not only by air pollutants emitted from the surrounding regional urban areas, but also by the long-range transport of air pollutants from East Asia due to the proximity of the study site to East Asia.

This study characterized the atmospheric nitrogen and sulfur containing compounds at a inland suburban-forested site in northern Kyushu, western Japan for one year 1) to investigate the effects of the pollutant emissions from the regional area and the long-range transport from East Asia on atmospheric concentrations of nitrogen and sulfur containing compounds and 2) to evaluate chemical forms of sulfate and nitrate particulates.

Table 1
National emissions of SO_2 and NO_x, and NH_3 (kt yr^{-1}).

	China	Japan	S. Korea	N. Korea	Taiwan	Mongolia	Reference
SO_2	27,555	926	986	297	266	88	Ohara et al. (2007)
	20,385	801	829	227	376	101	Streets et al. (2003)
NO_x^a	11,186	1959	1559	221	648	41	Ohara et al. (2007)
	11,347	2198	1322	273	521	221	Streets et al. (2003)
NH_3	13,570	352	172	98	152	155	Streets et al. (2003)

Data are in 2000 for Ohara et al. (2008) and Streets et al. (2003).
[a] Calculated as NO_2.

2. Materials and methods

2.1. Site description

This study was conducted at the inland suburban-forested site (33° 38′N, 130° 31′E, 70 masl) in Sasaguri Town located 15 km east of the city of Fukuoka in Fukuoka Prefecture, western Japan (Fig. 1). The population density of the town of Sasaguri is 807 people km^{-2} (31,000 people, 39 km^2 area). There are no large anthropogenic emission sources of air pollutants near the study site, because emissions of SO_2 and NO_x from Sasaguri and the town of Hisayama are small (Table 2). The mean annual precipitation and mean annual temperature observed from 1998 to 2004 were 1586 mm (range: 1249–1973 mm/year) and 16.2 °C (range: from 5.5 °C in January to 26.9 °C in August monthly average), respectively.

2.2. Collection of atmospheric gaseous and particulate compounds

Three annular denuders (URG-2000-30 × 242-3CSS, USA) in series followed by a filter pack (URG-2000-30F, USA) were used for the collection of gaseous (HNO$_3$, HNO$_2$, SO$_2$, and NH$_3$) and particulate (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, and Ca^{2+}) compounds. The first and second denuders were coated with Na$_2$CO$_3$ (1% w/v + 1% glycerol in a 1:1 methanol/water solution), and the third with citric acid (1% w/v in
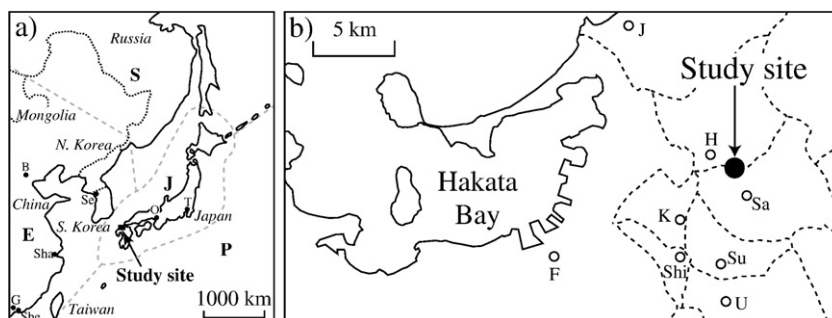

Fig. 1. Location of the study site and sector classification (E, J, S, and P) for backward trajectory analysis. Letters of E, J, S, and P indicate East Asia, Japan, Siberia, Pacific Ocean, respectively. Short-dashed lines in a) indicate national boundaries. B, G, O, Se, Sha, She, and T indicate Beijing, Guangdong, Osaka-Kobe, Seoul, Shanghai, Shenzhen, and Tokyo, respectively, which are among the 30 largest urban agglomerations ranked by population size in the world in 2005 (United Nations, 2007). Short-dashed lines in b) indicate municipal boundaries. F, J, Shi, Su, U, H, and Sa indicate the city of Fukuoka, the town of Shingu, the town of Kasuya, the town of Shime, the town of Sue, the town of Umi, the town of Hisayama, and the town of Sasaguri, respectively. Referred national emissions of SO_2, NO_x and NH_3 are shown in Table 1 and municipal emissions of SO_2 and NO_x are shown in Table 2.

Table 2
Municipal emissions of SO_2 and NO_x (kt yr^{-1}).

	Fukuoka	Shingu	Kasuya	Shime	Sue	Umi	Hisayama	Sasaguri
SO_2	1.43	0.29	0.07	0.01	0.02	0.04	0.14	0.01
NO_x[a]	7.15	0.35	0.01	0.00	0.00	0.03	0.12	0.02

Data are in 2003 for Fukuoka City (Environmental Agency of Fukuoka City, 2006) and in 2005 for Jingu, Kasuya, Shime, Sue, Umi, Hisayama, and Sasaguri Towns (Ministry of Environment, 2008).

[a] Calculated as NO_2.

methanol). The first denuder was used to collect acidic gases, and the second to eliminate potential interference from NO_2 and other compounds in the atmosphere for the determination of atmospheric HONO that will be presented elsewhere. HNO_3 and SO_2 concentrations were determined from the first denuder and were not corrected from the second denuder. The rate of nitrate in the second denuder relative to that in the first denuder was 0.08 (± 0.05 standard deviation; $n = 54$) and was not significantly different among seasons. The capture efficiency of SO_2 calculated by dividing sulfate in the first denuder by that in the first and second denuders was 0.98 (± 0.03 standard deviation; $n = 54$) and was not significantly different among seasons. The third was to collect gaseous ammonia. A Teflon filter (Advantec T080A047A; pore size 0.8 µm) was used to collect particulates. No preimpactor was used so as to avoid any possible adsorptive losses. After the annular denuder tubes were coated with coating solution, the coated tubes were dried with N_2 gas at a rate of 3 l min^{-1}. The inlet was 1.5 m above the ground in the open at the sampling site. An air pump (SIBATA, MP-500) was used for sucking ambient air at a flow rate of 5 l min^{-1}.

Routine 24-hour bulk sampling was performed weekly starting in the evening (17:00–18:00) during the period from May 2006 to April 2007, and a total of 46 routine samples were collected. The sampling was performed once per week, starting usually from Wednesday to Thursday or from Thursday to Friday. In addition, an intensive 12-hour bulk sampling campaign was conducted for three consecutive days, separately for daytime and nighttime, in summer (7–10 August 2006), winter (19–22 February 2007), and spring (25–27 April 2007). Unfortunately, no data were available for 9 August 6:00–18:00 due to trouble with the air pump. Each sampling period lasted 12 h, from 6:00 to 18:00, or from 18:00 to 6:00. This allowed for 'daytime' and 'nighttime' comparisons to be made. The annual and seasonal mean concentrations of gaseous and particulate compounds were calculated from the data obtained from the routine 24-hour and intensive 12-hour bulk samplings.

A passive sampler (Ogawa, OG-SN-S, USA) impregnated with triethanolamine (TEA) was used for the determination of the daily ambient NO_2 concentration. Simultaneously, a chemiluminescent analyzer (Thermo Environmental Instruments, model 42S, USA) was used for the determination of NO_2 concentrations for the intensive 12-hour bulk sampling campaign. The daily NO_2 concentration (ppb) determined by the passive sampler (NO_{2p}) was well correlated with that determined by the chemiluminescent analyzer (NO_{2c}) on the same day ($NO_{2c} = 1.02 NO_{2p} + 1.69$; $r = 0.96$). However, it should be noted that the NO_2 concentration determined by the TEA passive sampler and TEI chemiluminescent analyzer includes some NO_y species. Ozone (O_3) concentrations were determined by UV absorption analyzers (Thermo Environmental Instruments, model 49C, USA). Data were recorded at 10-minute intervals by a datalogger (Campbell, CR-10X, USA). O_3 concentrations were determined during August 2006, October 2006, February 2007, March 2007, and April 2007 for 24-hour routine bulk sampling (12 days) and the intensive 12-hour bulk sampling campaign (8 days).

2.3. Chemical analysis and calculation

After sampling, each annular tube was extracted twice with 10 ml of distilled water. The extracted solution was stored in a refrigerator at 4 °C before chemical analysis. Teflon filter was extracted with 30 ml of distilled water in a polypropylene bottle by ultra-sonication for 1 h. Ions in the extract solutions were analyzed by ion chromatography (Dionex, DX-120, USA). For the separation of anions, an anion exchange column (Ionpac AS14, Dionex, USA) and a self regenerating suppressor (Dionex, ASRS-Ultra II, USA) were used. The eluent was a mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$, and the flow rate was 1.0 ml min^{-1}. Fifty µl of extract solution was injected. For the separation of cations, a cation exchange column (Ionpac CS12A, Dionex, USA) and a self regenerating suppressor (Dionex, CSRS-Ultra II, USA) were used. The eluent was 20 mmol l^{-1} methanesulfonic acid, and the flow rate was 1.0 ml min^{-1}. One hundred µl of filtered sample was injected. Detection limits for Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} were 7.8, 16.3, 19.7, 3.0, 5.8, 5.1, 4.4, and 6.5 µg l^{-1}, respectively. Reproducibilities were 1.3%, 1.9%, 1.3%, 0.7%, 1.7%, 0.8%, 0.4%, and 0.8%, respectively. The filter impregnated with TEA for the determination of daily ambient NO_2 concentration was extracted with 8 ml of distilled water in a polyethylene bottle for 15 min. Nitrite (NO_2^-) in the extracted solutions was then immediately analyzed by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride.

Atmospheric concentrations (µg m^{-3}) of HNO_3, SO_2, NH_3, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were calculated by multiplying concentrations determined (µg l^{-1}) by the volume extracted (l) and dividing by the air volume drawn (m^3) during the sampling period. Preliminary experiments were conducted to consider the field blanks of the annular denuder sampling systems. The "field blank filter packs" were connected to the sampling system and air was drawn through the filters for 10 s. The field blanks for HNO_3, SO_2, NH_3, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were 0.33 µg, 0.26 µg, 0.11 µg, 0.23 µg, 0.49 µg, 0.59 µg, 0.09 µg, 0.17 µg, 0.15 µg, 0.13 µg, and 0.20 µg, respectively. Therefore, detection limits of HNO_3, SO_2, NH_3, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} for the sampling system in this study were 0.05 µg m^{-3}, 0.04 µg m^{-3}, 0.02 µg m^{-3},

0.03 µg m^{-3}, 0.07 µg m^{-3}, 0.08 µg m^{-3}, 0.01 µg m^{-3}, 0.02 µg m^{-3}, 0.02 µg m^{-3}, 0.02 µg m^{-3}, and 0.03 µg m^{-3}, respectively for 24-hour bulk sampling. The concentrations of non-sea salt (nss)-SO_4^{2-} and nss-Ca^{2+} were calculated from the equivalent ratios of SO_4^{2-}/Na^+ (0.0603) and Ca^{2+}/Na^+ (0.0214) in seawater. The nitrogen conversion ratio (F_n) and sulfur conversion ratio (F_s) were defined as follows, respectively (Khoder, 2002).

$$F_n = \frac{NO_3^-(g) + NO_3^-(p)}{NO_2 + NO_3^-(g) + NO_3^-(p)},$$

$$F_s = \frac{nss - SO_4^{2-}(p)}{SO_2 + nss - SO_4^{2-}(p)},$$

Where $NO_3^-(g)$, $NO_3^-(p)$, NO_2 represent the gaseous nitric acid, nitrate, and nitrogen dioxide concentrations, as NO_2, µg m^{-3}, respectively, and nss-$SO_4^{2-}(p)$, and SO_2 represent non-sea salt sulfate and sulfur dioxide concentration, as SO_2, µg m^{-3}, respectively.

2.4. Meteorological parameters

Meteorological parameters, such as precipitation, wind speed/direction, temperature, and relative humidity, were continuously measured at the study site. Precipitation was measured by a tipping-bucket rain gauge (Takeda Instruments, TK-1, certificated, Japan). Wind speeds and direction were monitored 10 m above the ground by an anemometer (R. M. Young Company, Model 05103-47, USA) and vane (R. M. Young Company, Model 05103-47, USA), respectively. Temperature and relative humidity 2 m above the ground were measured by relative humidity and temperature probes with a solar radiation shield (Vaisala, DTR503A, Finland). Data were recorded at 10-minute intervals by a datalogger (Campbell, CR-10X, USA).

2.5. Backward trajectories

Backward trajectory analysis was performed using the hybrid single-particle Lagrangian integrated trajectory (Hy-SPLIT 4) model (Draxler and Rolph, 2003; Rolph, 2003) for each sampling day. The trajectories were calculated five times a day at 0900, 1500, 2100, 0300, and 0900 GMT when air sampling was conducted. Three day backward trajectories, using as input the meteorological data fields supplied by the National Meteorological Center Global Data Assimilation System were calculated, ending 100 m above the ground. The trajectories were classified into four sectors according to the modification of Yoshioka et al. (2009) as shown in Fig. 1, on the basis of air masses mainly from East Asia (E), Siberia (S), Japan (J) and the Pacific Ocean (P).

3. Results and discussion

3.1. N containing components

The annual mean concentration of HNO_3 at the study site (Table 3) was comparable to values determined in urban areas in Japan and other countries (Table 4). Atmospheric HNO_3 is a major contributor to dry deposition of nitrogen to a forest canopy (Bytnerowicz et al., 1987; Andersen and Hovmand, 1999; Sievering et al., 2001; Tarnay et al., 2001; Bytnerowicz et al., 2002; Chiwa et al., 2008) owing to the high deposition velocity characteristics of HNO_3 (Fenn and Bytnerowicz, 1993; Hoek et al., 1996; Andersen and Hovmand, 1999; Bytnerowicz et al., 2002). Dry deposition to the forest canopy can be estimated by multiplying the measured air concentrations by the deposition velocities (Hanson and Lindberg, 1991; Tarnay et al., 2001). Higher HNO_3 concentration at this study indicated that dry deposition of nitrogen to the forest canopy is enhanced at the study site compared with other forested areas with lower atmospheric concentrations of HNO_3.

The HNO_3 concentration had a diurnal variation, being higher in daytime and lower at night (Table 5). The diurnal variation of HNO_3 was also consistent with other studies (Khoder, 2002; Lin et al., 2006). HNO_3 is mainly produced by the reaction of NO_2 with OH during the daytime (Seinfeld and Pandis, 2006). Because the efficient removal of HNO_3 from the atmosphere limits the long-range transport of HNO_3 (Neuman et al., 2006), this diurnal variation could be due to regional production of HNO_3 during daytime. Fig. 2 shows the diurnal variations in the frequencies for wind speeds (W_s) and directions (W_d) at the study site. Wind speeds were higher during the daytime than during the nighttime. In addition, wind from SW-W-NW typically dominated during the daytime and wind from NE-E-SE prevailed during the nighttime. This diurnal variation of wind speed/direction was observed for all seasons, but it slightly differed for fall daytime, summer nighttime and spring nighttime (Fig. 3). These results suggest that winds during the daytime mostly blew from the coast to the study site. This diurnal variation of wind speed/direction suggested that air pollutants emitted from the regional urban area located in the coastal area (Fukuoka urban area) were transported to the study site during the daytime. In addition, it is suggested that HNO_3 was produced in the coastal urban area and/or during transport from the coastal urban area to the study site during the daytime, leading to the higher HNO_3 concentration at the study site.

The HNO_3 concentration was significantly higher in summer than in winter (Table 3), which is consistent with other studies (Solomon et al., 1992; Hong et al., 2002; Khoder, 2002; Bari et al., 2003; Chiwa et al., 2008). However, the HNO_3 concentration in spring was comparable to that in summer in this study. The nitrogen conversion ratio (F_n) significantly correlated with ozone (O_3) concentration (Fig. 4a; $P < 0.01$). A significant correlation between the F_n value and O_3 concentration was consistent with other studies (Kadowaki, 1986; Lin et al., 2006), and supports the formation of HNO_3 by the reaction of NO_2 with OH radical derived from the photolysis of O_3 (Creasey et al., 2001; Seinfeld and Pandis, 2006). The concentration of O_3 in spring was somewhat higher (Table 5). Therefore, the increased reaction between NO_2 and hydroxyl radicals (OH·) in spring during the daytime is one of the reasons for the concentration of HNO_3 in spring being comparable to that in summer.

Another reason could be increased removal of HNO_3 by rainfall in summer compared with that in spring due to the lower rainfall during spring. Rainfall can remove gaseous compounds such as HNO_3 from atmosphere. This study showed that HNO_3 concentrations in spring and summer were significantly lower when rainfall events occurred during

Table 3

Summary of mean concentrations of gaseous and particulate compounds measured at the Kasuya Research Forest from May 2006 to April 2007[1].

	HNO$_3$	SO$_2$	NH$_3$	NO$_2$	Cl$^-$	NO$_3^-$	nss-SO$_4^{2-}$	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	nss-Ca^{2+}	F$_n$[4]	F$_s$[5]
	µg m^{-3}												%	
All (May 06–Apr 07)														
Mean	2.16	7.01	0.79	16.01	0.67	2.02	8.47	0.84	3.07	0.36	0.13	0.40	17.4	44.3
Median	1.89	6.23	0.70	15.81	0.43	1.86	6.45	0.71	2.43	0.26	0.12	0.33	16.0	44.5
Min	0.34	1.22	0.13	5.84	0.16	0.25	1.04	0.08	0.39	ND[3]	ND	ND	2.2	17.4
Max	5.24	21.73	2.73	34.83	6.24	8.31	31.55	1.98	10.49	0.45	0.27	0.53	36.7	70.0
S.D.	1.23	4.41	0.46	7.57	1.27	1.47	6.25	0.40	2.09	0.11	0.06	0.11	8.2	13.2
n	54	54	54	54	54	54	54	54	54	54	54	54	51	54
Summer (Jun 06–Aug 06)														
Mean	2.55 b[2]	3.85 a	1.11 c	15.33 a	0.42 a	1.05 a	6.37 a	0.65 a	1.75 a	0.23 a	0.07 a	0.13 a	17.1 ab	49.0 b
Median	1.93	3.74	1.11	14.21	0.29	1.00	3.68	0.64	1.05	0.18	0.07	0.11	17.6	49.9
Min	0.55	1.22	0.43	5.84	0.09	0.25	1.04	0.12	0.39	0.03	0.00	0.01	2.2	26.4
Max	5.24	6.59	2.40	29.93	1.32	2.07	16.42	1.35	4.65	0.56	0.14	0.31	34.2	62.4
S.D.	1.66	1.96	0.50	8.50	0.37	0.56	4.98	0.37	1.39	0.18	0.04	0.11	9.3	11.5
n	12	12	12	12	12	12	12	12	12	12	12	12	12	12
Fall (Sep. 06–Nov. 07)														
Mean	2.17 ab	5.73 ab	0.84 bc	15.72 a	0.66 a	1.82 ab	8.91 a	0.87 a	2.97 a	0.42 a	0.15 ab	0.45 b	15.6 a	48.9 b
Median	2.18	5.98	0.85	16.57	0.54	1.89	6.21	0.77	2.05	0.39	0.12	0.42	13.5	51.6
Min	0.94	2.76	0.27	7.34	0.10	0.88	3.43	0.25	0.74	0.18	0.05	0.18	9.3	26.5
Max	3.62	10.71	1.35	27.67	2.69	3.14	18.79	2.20	6.63	1.07	0.37	0.81	22.6	67.0
S.D.	0.85	2.41	0.31	6.42	0.68	0.64	5.56	0.52	2.20	0.27	0.08	0.21	5.1	10.7
n	12	12	12	15	12	12	12	12	12	12	12	12	12	12
Winter (Dec. 06–Feb 07)														
Mean	1.28 a	7.94 b	0.40 a	18.11 a	0.89 a	2.11 ab	6.62 a	0.89 a	2.29 a	0.34 a	0.15 ab	0.42 b	13.1 a	35.5 a
Median	1.04	7.73	0.43	16.94	0.40	2.02	6.18	0.60	2.23	0.24	0.12	0.33	12.8	34.7
Min	0.34	2.40	0.11	6.97	0.21	0.52	2.32	0.13	0.77	0.16	0.04	0.09	2.9	25.3
Max	3.58	12.61	0.67	34.83	3.57	4.81	14.42	2.66	4.39	0.87	0.35	0.92	22.6	59.6
S.D.	0.85	3.26	0.17	8.30	1.03	1.16	3.52	0.71	1.06	0.23	0.10	0.23	5.6	10.3
n	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Spring (May 06, Mar 07–Apr 07)														
Mean	2.61 b	9.49 b	0.53 ab	14.70 a	0.69 a	2.82 b	11.31 a	0.93 a	3.64 a	0.44 a	0.16 b	0.53 b	24.0 b	45.0 ab
Median	2.50	8.90	0.47	11.11	0.47	2.08	7.80	0.75	2.73	0.31	0.16	0.47	25.0	45.0
Min	1.01	1.75	0.20	6.59	0.15	0.34	3.29	0.19	1.03	0.16	0.01	0.01	8.4	17.4
Max	4.59	21.70	0.98	28.43	2.71	8.31	31.55	2.85	10.49	1.09	0.42	1.32	36.7	70.0
S.D.	1.04	5.96	0.21	7.52	0.65	2.12	8.42	0.63	2.77	0.30	0.10	0.34	8.5	15.4
n	16	16	16	13	16	16	16	16	16	16	16	16	13	16

1) Intensive 12-hour bulk samplings were included in these values. 2) Different letters indicate significant differences at $P<0.05$ (Tukey's HSD test) among season. 3) ND indicates not detected. 4) The nitrogen conversion ratio. 5) The sulfur conversion ratio.

sampling (1.7 ± 1.2 µg m^{-3}) than when no rainfall occurred (3.0 ± 1.3 µg m^{-3}) ($P=0.041$). The amount of rainfall at the study site was considerably higher in summer (1212 mm) than that in spring (329 mm).

O$_3$ concentration in spring nighttime was comparable to that in spring daytime (Table 5). A backward trajectory analysis revealed the predominance of air masses flowing from East Asia in spring (Fig. 5), suggesting that the higher concentration of O$_3$ in spring may be due to long-range transport from East Asia. In support of this view, O$_3$ concentration was higher in spring in western Japan (Wakamatsu et al., 1998; Ohara et al., 2001; Fujihara et al., 2003; Itano et al., 2006), which is not only due to the intrusions from stratospheric ozone (Wakamatsu et al., 1989) but also due to the long-range transport from East Asia (Satsumabayashi et al., 1998; Wakamatsu et al., 1998; Ohara et al., 2001; Fujihara et al., 2003; Tanimoto et al., 2005; Itano et al., 2006; Suthawaree et al., 2008). In spring 2007, higher O$_3$ concentration (more than 100 ppb) was observed in Fukuoka city, around which this study was conducted. This was mainly due to the long-range transport of air pollutants from East Asia

(Iwamoto et al., 2008; Kurokawa et al., 2008; Ohara et al., 2008). As shown in Fig. 4a, a higher concentration of O$_3$ promotes the photoformation of HNO$_3$. On the basis of a typical concentration of OH radical in tropospheric atmosphere (1×10^6 molecules cm^{-3}: Seinfeld and Pandis, 2006), NO$_2$ concentration in spring season in this study site (approximately 15 µg m$^{-3} = 2 \times 10^{11}$ molecules cm^{-3}; Table 3), and rate constants of ($\sim 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} 300 K and 1 atm: Seinfeld and Pandis, 2006), I calculated HNO$_3$ production rate during daytime to be 0.55 µg m^{-3} h^{-1}. Because the study site is located 10–15 km east of coastal urban area, it takes 1.4–2.1 h for air mass in coastal urban area to arrive at the study site, if wind speed is 2 m s^{-1} that was observed during spring daytime in this study (Figs. 2, 3). Then, HNO$_3$ production was calculated to be 0.8–1.1 µg m^{-3}, which can explain the competitive concentration of HNO$_3$ in spring to that in summer in this study. Therefore, it is suggested the higher concentration of O$_3$ derived mainly from the long-range transport from East Asia enhanced regional HNO$_3$ production via the reaction of NO$_2$ emitted from the coastal urban area in spring.

Table 4
A comparison of average concentrations of gaseous HNO_3, SO_2, NH_3, NO_3^-, SO_4^{2-}, and NH_4^+ in forested and other locations in Japan and elsewhere.

Location		Period	Concentration ($\mu g\ m^{-3}$)						Method	Reference
			HNO_3	SO_2	NH_3	NO_3^-	SO_4^{2-}	NH_4^+		
Japan										
Mt. Oyama, Kanagawa	Mountain	Jan.–Dec. 1995	0.76	0.61	0.85	1.80	5.33	2.32	FP[2]	Igawa et al. (1998)
Nara	Suburban	June 1994–May 1995	1.61	4.32	2.43	2.09	4.27	1.70	AD–FP	Matsumoto and Okita (1998)
Dazaifu, Fukuoka	Urban/suburban	8–27 Jan. 1997	1.65	21.05	3.59	5.98	6.36	4.55	FP	Shimohara et al. (2001)
Goto, Nagasaki	Remote island	8–27 Jan. 1997	0.26	4.40	0.17	1.60	4.17	1.21	FP	Shimohara et al. (2001)
Mt. Gokurakuji, Hiroshima	Mountain (urban-facing)	Nov. 2002–Oct. 2003	1.64	2.54		0.64	2.80		FP	Chiwa et al. (2008)
Mt. Gokurakuji, Hiroshima	Mountain (mountain-facing)	Nov. 2002–Oct. 2003	0.67	1.20		0.37	2.00		FP	Chiwa et al. (2008)
Korea										
Seoul	Urban	Nov. 1996–Dec. 1998	2.30		3.95	4.83	4.88		FP	Hong et al. (2002)
Chunchon	Rural	Sep. 1996–Dec. 2000	1.70	7.30	3.07	5.70	5.80	2.83	FP	Hong et al. (2002)
Seoul	Urban	Oct 1996–Sep 1997	1.09	17.30	4.34	5.97	8.70	4.19	AD–FP	Lee et al. (1999)
Taiwan										
Taichung	Urban	Jan 2002–Dec 2002	1.9		8.5	6.0		4.6	AD–FP	Lin et al. (2006)
Pakistan										
Lahore	Urban	Dec 2005–Feb 2006	1.00	19.4	50.1	18.9	19.2	16.1	AD–FP	Biswas et al. (2008)
U.S.A										
Manhattan, New York	Urban	July 1999–June 2000	1.65	28.38	3.48		4.24		AD–FP[3]	Matsumoto and Okita (1998)
Ash Mountain, California	National Park	May–Nov 1999	2.10	1.30	4.50	1.30	0.60	1.30	AD–FP	Bytnerowicz et al. (2002)
Barton Flats, California	Mountain	Nov 1991–Sep 1993	0.70	0.50	1.45	2.30	0.97	0.63	AD–FP	Watson et al. (1999)
Eastern North California	Farm	Sep–Dec 1997	0.15	2.99	10.48	0.55	3.25	1.10	AD–FP	McCulloch et al. (1998)
Egypt										
Dokki, Giza	Urban	Dec 1999–Feb 2000	3.90	104.00		8.00	20.16		FP	Khoder (2002)
Austria										
Wolkersdorf	Rural	Nov. 1990–Otc. 1991	1.78	15.60	1.49	4.60	8.20	4.55	AD–FP	Puxbaum et al. (1993)
Turkey										
Küçük Çalticak, Antalya	Urban	Aug. 1995–Apr. 1996[1]	0.42	2.03	0.99	2.28	2.35	2.19	FP	Erduran and Tuncel (2001)

[1]17 March–21 April 1997 for nitric acid. [2]FP: filter pack. [3]AD–FP: annular denuder–filter pack.

The NO_3^- concentration and F_n value were significantly higher in spring than in other seasons (Table 3). In addition, the NO_3^- concentration and F_n value in spring nighttime were comparable to those in spring daytime (Table 5). As mentioned above, backward trajectory analysis revealed a predominance of air mass flowing from East Asia in spring (Fig. 5). Fig. 6 shows

Table 5
Average daytime and nighttime concentrations of nitrate and sulfur containing compounds measured at the Kasuya Research Forest.

Season	n daytime/ nighttime	HNO_3 $\mu g\ m^{-3}$			SO_2			NH_3			NO_2			Cl^-			NO_3^-			nss-SO_4^{2-}		
		D	N	D/N[a]	D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N
Summer	2/3	8.55	0.96	8.9	5.93	3.46	1.7	2.03	0.60	3.4	15.9	16.5	1.0	0.58	0.69	0.8	1.26	0.81	1.6	12.8	9.0	1.4
Winter	3/3	2.62	0.72	3.7	9.81	9.89	1.0	0.54	0.21	2.6	23.8	20.7	1.2	0.38	0.36	1.0	2.17	2.36	0.9	6.82	6.64	1.0
Spring	3/3	4.76	1.64	2.9	16.7	19.7	0.8	0.83	0.53	1.6	16.8	17.2	1.0	0.51	0.51	1.0	4.86	5.20	0.9	22.8	25.8	0.9
All		5.31	1.11	4.8	10.8	11.0	1.0	1.13	0.45	2.5	18.8	18.1	1.0	0.49	0.52	0.9	2.76	2.79	1.1	14.1	13.8	1.1

Season	n daytime/ nighttime	Na^+ $\mu g\ m^{-3}$			NH_4^+			Mg^{2+}			nss-Ca^{2+}			O_3			F_n^a			F_s^b		
		D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N	D	N	D/N
Summer	2/3	0.68	0.44	1.6	3.61	2.83	1.3	0.06	0.07	0.9	0.24	0.16	1.5	45.7	15.0	3.1	31.3	7.20	4.3	59.4	64.8	0.9
Winter	3/3	0.58	0.49	1.2	2.31	2.53	0.9	0.17	0.15	1.1	0.57	0.64	0.9	34.6	25.6	1.4	12.9	10.0	1.3	32.8	31.6	1.0
Spring	3/3	0.99	0.76	1.3	7.33	8.91	0.8	0.21	0.16	1.3	1.13	0.83	1.4	65.3	55.2	1.2	29.4	23.0	1.3	46.7	47.0	1.0
All		0.75	0.56	1.3	4.42	4.75	1.0	0.14	0.13	1.1	0.65	0.54	1.2	48.5	31.9	1.9	24.5	13.4	2.3	46.3	47.8	1.0

[a]Ratio of daytime value over nighttime value. [b]The nitrogen conversion ratio. [c]The sulfur conversion ratio.
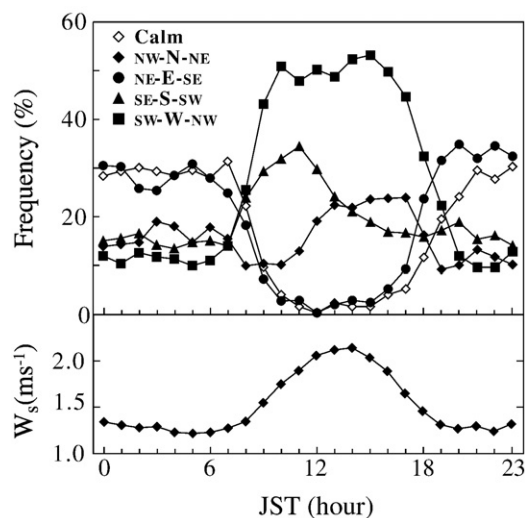
Fig. 2. Diurnal variations of frequencies for wind direction and hourly average wind speeds at the study site. Wind direction was classified by NNW-N-NE, ENE-E-SE, SSE-S-SW, and WSW-W-NW. Calm was defined as $W_s < 0.4$ ms^{-1}. Periods of data presented are from May 2006 to April 2007.

the NO$_3^-$ concentration is higher when air mass was transported from East Asia. These results suggest HNO$_3$ is produced during the transport from East Asia, and some of the HNO$_3$ is subsequently neutralized to form NO$_3^-$ during transport to the study site in spring. Thus, the long-range transport from East Asia considerably contributed to a higher concentration of NO$_3^-$ in spring. The formation of NO$_3^-$ is caused by the reaction of HNO$_3$ with NH$_3$ mainly in agricultural areas (Shimohara et al., 2001; Morino et al., 2006; Seinfeld and Pandis, 2006), with sea-salt particles such as Na$^+$, and with soil-derived nss-Ca^{2+} (Matsumoto et al., 1998; Jordan et al., 2000; Shimohara et al., 2001; Hanisch and Crowley, 2001; Hatakeyama et al., 2004; Arnold and Luke, 2007) during air mass transport. In spring, dust storms in East Asia are frequently observed and play a significant role in the heterogeneous conversion of HNO$_3$ to NO$_3^-$ (Ooki and Uematsu, 2005, Matsumoto et al., 2003, Takiguchi et al., 2008). The chemical form of NO$_3^-$ will be discussed later.

3.2. S containing components

The annual mean concentrations of SO$_2$ and nss-SO$_4^{2-}$ at the study site (Table 3) were higher than those determined in urban areas and forested areas near urban areas in Japan and other countries (Table 4). Therefore, higher concentrations of SO$_2$ and nss-SO$_4^{2-}$ in this study suggested that dry deposition of sulfur to a forest canopy is higher at the study site than elsewhere, as is dry deposition of nitrogen.

SO$_2$ concentration was significantly higher in winter and spring than in summer (Table 3). It is shown that air mass flowing from East Asia was predominant in winter and spring (Fig. 5) and the SO$_2$ concentration was higher when air mass was transported from East Asia (Fig. 6). Therefore, it is suggested the long-range transport of SO$_2$ from East Asia in winter and spring caused the higher concentration of SO$_2$ at the study site.

In addition, the F_s value was significantly lower in winter. This result indicates the reduced oxidation of SO$_2$ to SO$_4^{2-}$ in winter, which is one of the possible reasons for the higher concentration of SO$_2$ in winter at the study site. Furthermore, lower boundary layer heights and higher emissions of sulfur which are observed exclusively in winter (Lin et al., 2008), are other possible reasons for the higher SO$_2$ concentrations in winter.

The nss-SO$_4^{2-}$ concentration was also higher when air mass was transported from East Asia (Fig. 6). It has been shown that a higher concentration of nss-SO$_4^{2-}$ in Japan was caused by long-range transport from East Asia in winter (Shimohara et al., 2001) and spring (Uematsu et al., 2002; Matsumoto et al., 2003). Therefore, it is likely the long-range transport of nss-SO$_4^{2-}$ from East Asia in winter and spring also caused the higher concentration of nss-SO$_4^{2-}$ at the study site.

However, there was no statistical seasonal variation of the nss-SO$_4^{2-}$ concentration because the concentration of nss-SO$_4^{2-}$ in summer was comparable to the concentrations in winter and spring (Table 3). Backward trajectory analysis revealed a predominance of air mass flowing into the study area from Japan in summer (Fig. 5), suggesting the higher concentration of nss-SO$_4^{2-}$ in summer was not caused by the long-range transport from East Asia. The F_s value was significantly higher in summer than in winter (Table 3). These results indicate the increased oxidation of SO$_2$ to SO$_4^{2-}$ in summer, which is a probable reason for the comparable concentration of nss-SO$_4^{2-}$ in summer at the study site.

In contrast to the significant correlation between F_n and O$_3$, F_s values were not significantly correlated with O$_3$ concentrations (Fig. 4b). Instead, there were weak but significant relationships between F_s values and relative humidity (Fig. 7a) and temperature (Fig. 7b). It was found that the droplet-phase reaction is important for SO$_2$ oxidation to SO$_4^{2-}$ when the O$_3$ concentration is more than 20 ppb (Kadowaki, 1986; Takeuchi et al., 2004). Because the O$_3$ concentration was more than 20 ppb at the study site, variation in O$_3$ concentration could not be a critical factor for the variation of F_s at the study site. Instead, meteorological parameters, such as higher relative humidity and temperature in summer are important factors for the increased oxidation of SO$_2$ to SO$_4^{2-}$ in summer. Oxidation of SO$_2$ by atmospheric peroxide (H$_2$O$_2$) is important for pH <5, while oxidation by O$_3$ is important at higher pH (Sakugawa et al., 1990; Seinfeld and Pandis, 2006). Atmospheric hydrogen peroxide plays an important role as an oxidizer of SO$_2$ to SO$_4^{2-}$ in particular in the aqueous-phases oxidation reactions (Sakugawa et al., 1990; Seinfeld and Pandis, 2006), because mean rainwater pH at a site approximately 2 km east of the study area was 4.6 (Chiwa et al., 2007). Since gaseous H$_2$O$_2$ has a large Henry's law constant, it can partition into aqueous-phase such as clouds, which could then oxidize SO$_2$ to SO$_4^{2-}$. Unfortunately, atmospheric H$_2$O$_2$ was not measured in this study. The atmospheric concentration of H$_2$O$_2$ is reportedly higher in summer due to higher photochemical formation caused by higher solar radiation and temperature, and higher water vapor content (Sakugawa et al., 1990).

Although oxidation of SO$_2$ to SO$_4^{2-}$ increased in summer at the study site partly owing to higher relative humidity and temperature in summer, F_s value was higher even in winter (35% ± 10%) than reported values in urban areas (7%: Kadowaki,
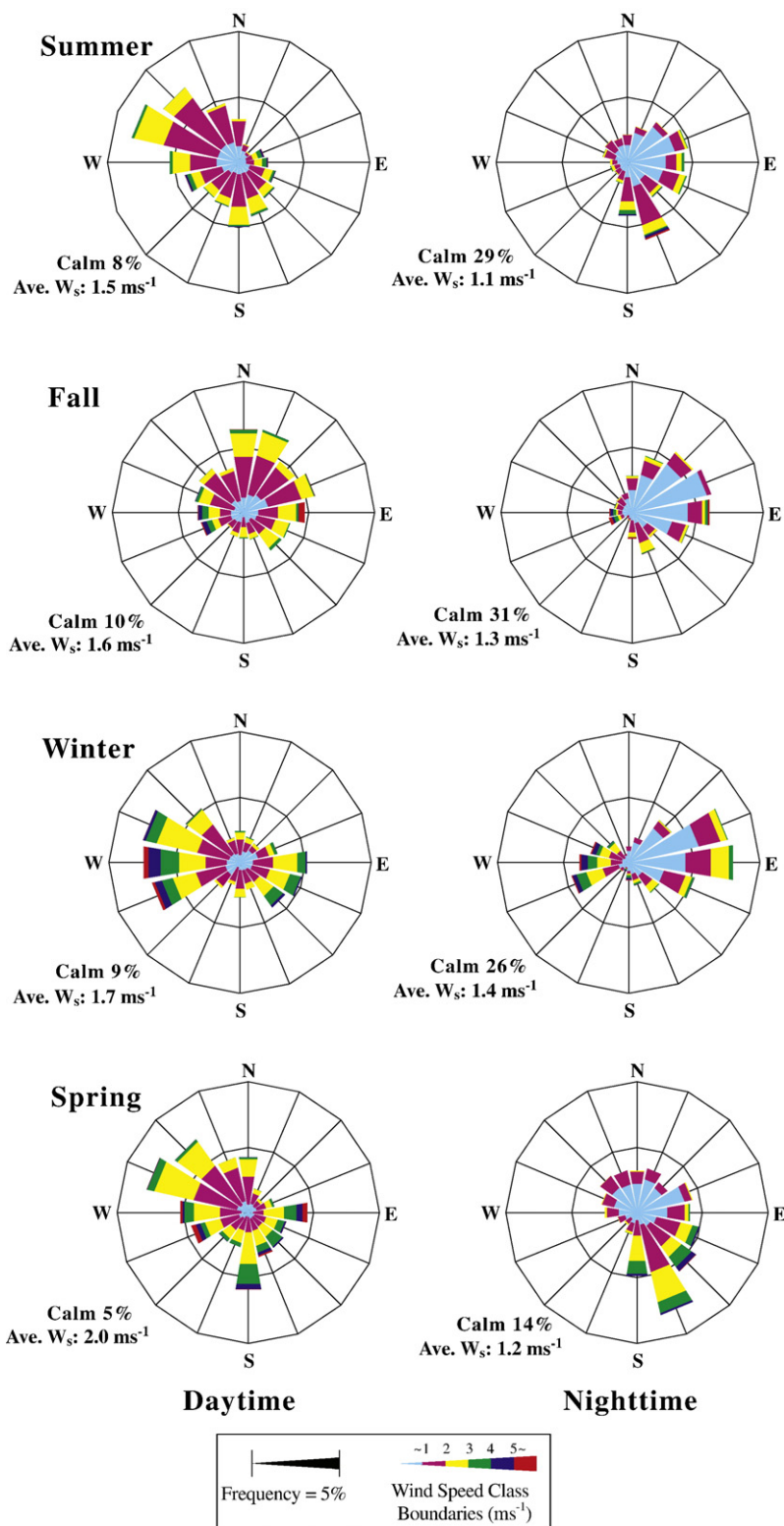
Fig. 3. Wind rose diagram for the study site. Periods of data presented are from May 2006 to April 2007.

1986; 18%: Shimohara et al., 2001; 12%: Khoder, 2002; 12%: Takeuchi et al., 2004; and 28%: Aikawa et al., 2005), and was comparable to reported values in rural areas (65%: Satsuma-

bayashi et al., 1999; 40%: Shimohara et al., 2001; and 35% Hong et al., 2002). A higher F_s value throughout the year at the study site indicates increased oxidation of SO_2 to SO_4^{2-}. Higher F_s
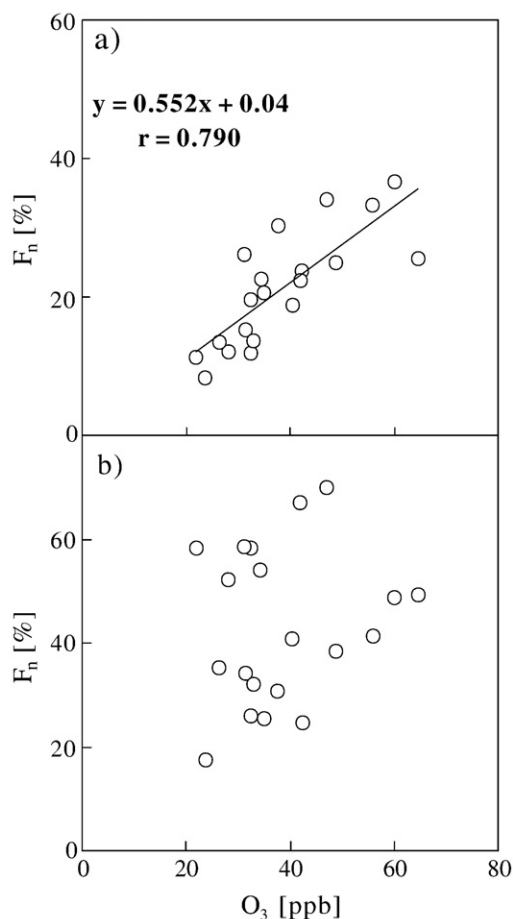
Fig. 4. Relationships between daily ozone (O_3) concentration and a) daily nitrogen conversion ratio (F_n) and b) daily sulfur conversion ratio (F_s). Daily concentration of O_3 was calculated from the 10-minute interval data, corresponding to 24-hour bulk sampling. Daily F_n and F_s values were calculated from two intensive 12-hour bulk samplings, daytime (6:00–18:00) and nighttime (18:00–6:00).
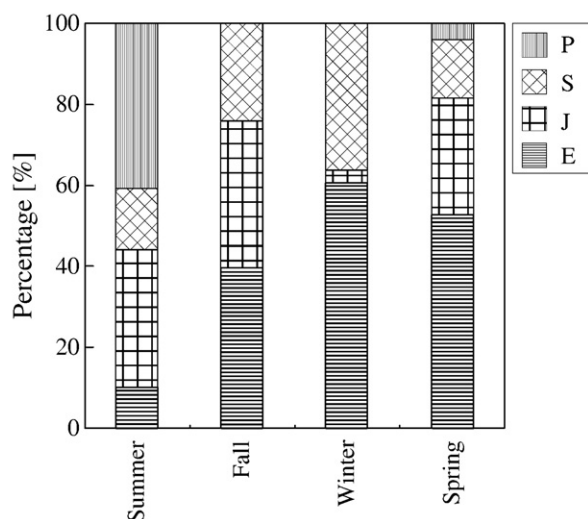
Fig. 5. Frequency of air trajectories of air masses that reached the study site. Letters of P, S, J, and E indicate sector classification (Pacific Ocean, Siberia, Japan, and East Asia, respectively) for backward trajectory analysis.
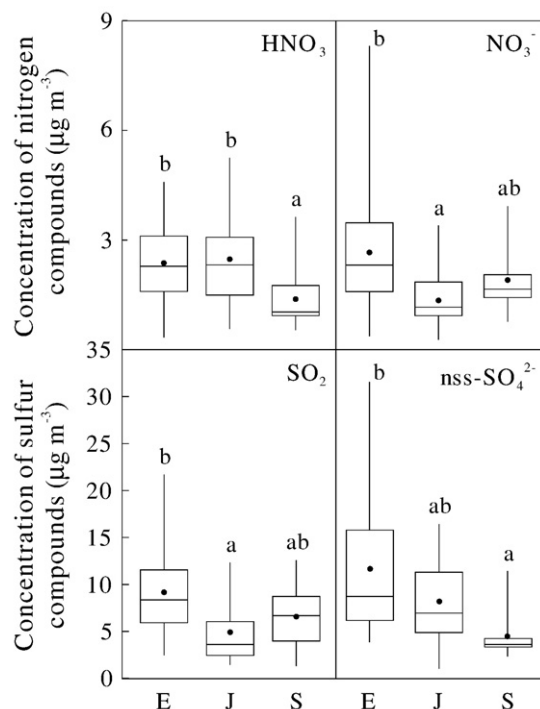
Fig. 6. Concentrations of HNO_3, NO_3^-, SO_2, and nss-SO_4^{2-} sorted according to the trajectory pathways shown in Fig. 1. Letters of S, J, and E indicate sector classification (Siberia, Japan, and East Asia, respectively) for backward trajectory analysis. Concentrations from Pacific Ocean (P) were not shown due to insufficient number for statistical analysis. In each box plot, the boundary of the box closest to zero indicates the 25th percentile, the closed circle represents the average, the solid line represents the median, and the boundary of the box farthest from zero represents the 75th percentile. Bars above and below the boxes indicate the maximum and minimum, respectively. Different letters indicate significant differences at $P<0.05$ (Tukey's honest significant difference test) among sectors.

values were caused by increased oxidation of SO_2 to SO_4^{2-} owing to the longer residence time of SO_4^{2-} (Satsumabayashi et al., 1998; Satsumabayashi et al., 1999). Because nss-SO_4^{2-} has a relatively long life time (Seinfeld and Pandis, 2006), higher values of F_s at the study sites throughout the year are probably due to the long time needed for SO_2 to oxidize to SO_4^{2-}, which supports the long-range transport of nss-SO_4^{2-} not only from East Asia but also from other areas.

In addition, the F_s values did not exhibit a diurnal variation in any season (Table 5). In contrast to the study site, Khoder (2002) showed F_s values were higher in the daytime than in the nighttime in an urban area. A higher F_s value in the daytime in an urban area is probably due to the local oxidation of SO_2 emitted from local urban area to SO_4^{2-} during the daytime. The different diurnal variations of F_s would be caused by different emissions of sulfur from various surrounding areas. No diurnal variation of F_s values at the study site also suggests the long-range transport of nss-SO_4^{2-} not only from East Asia but also from other areas.

3.3. Chemical form of sulfate and nitrate particulates

The frequency of the equivalent ratio of NH_4^+ and nss-SO_4^{2-} is shown in Fig. 8. The mean value of the equivalent ratio of
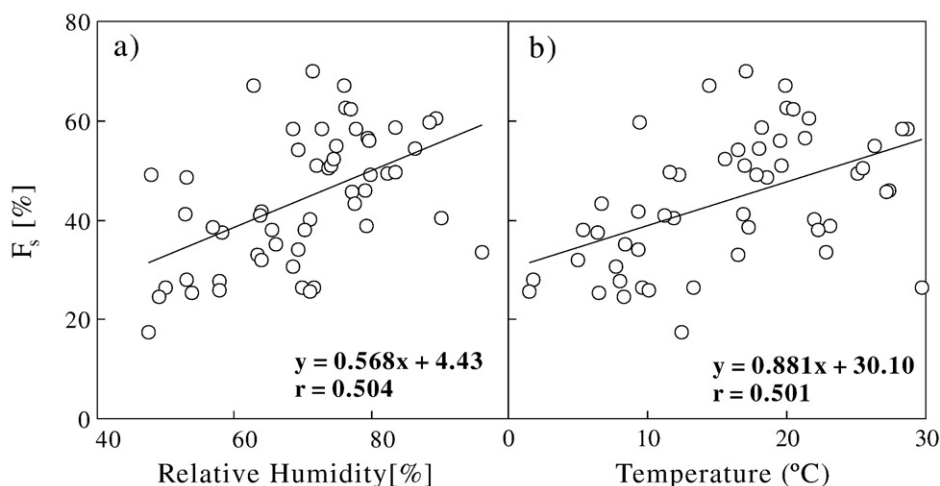
Fig. 7. Relationships between sulfur conversion ratio (F_s) and a) relative humidity and b) temperature.

NH_4^+ and nss-SO_4^{2-} was 0.96 ± 0.22 at the study site. This result indicates that acidic sulfate is neutralized by NH_3, existing mainly as $(NH_4)_2SO_4$ in fine particles because NH_3 preferentially reacts with H_2SO_4 over HNO_3 (Seinfeld and Pandis, 2006). If it is assumed a) there is incomplete neutralization of sulfate when the ratio is less than 0.80, b) there is complete neutralization of sulfate and no excess NH_4^+ associated with other compounds when the ratio is more than

Fig. 8. Frequency distribution of equivalent ratios of NH_4^+ and nss-SO_4^{2-} concentrations.

0.80 and less than 1.20, and c) there is complete neutralization of sulfate and excess NH_4^+ associated with other compounds when the ratio is more than 1.20, then the cases a, b, and c account for 24.1, 66.7, and 9.3% of the number of samples collected through the year, respectively. The limits of ± 0.20 along the 1:1 line were used to characterize the complete neutralization of sulfate and no excess NH_4^+ associated with other compounds because of uncertainties in determination of concentrations of nss-SO_4^{2-} and NH_4^+. This result suggested that acidic sulfate is neutralized by ammonia, existing mainly as $(NH_4)_2SO_4$ in fine particles.

In case c, NH_3 and HNO_3 are expected to be in equilibrium with NH_4NO_3 (solid or aqueous) in the atmosphere (Seinfeld and Pandis, 2006).

$$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4NO_3(s)$$
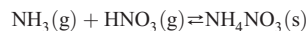
Case c accounted for only 9.3% of the number of samples (Fig. 8). The small percentage suggests NH_4NO_3 was not formed in most cases at the study site. NH_4NO_3 is the major form of NO_3^- in urban atmospheres where NH_3 emission is large (Shimohara et al., 2001; Morino et al., 2006; Seinfeld and Pandis, 2006). My results indicate the NH_3 preferentially reacted with acidic sulfate to form $(NH_4)_2SO_4$ and was no longer available for equilibration with NH_4NO_3 at the study site in most cases. This would be an additional reason for the higher concentration of HNO_3 at the study site.

On the other hand, there may be the possibility that nitrate is bound as a relatively non-volatile salt of Ca^{2+} or Na^+ as in the following.

$$NaCl + HNO_3 \rightarrow NaNO_3(s) + HCl(g)$$

$$CaCO_3 + 2HNO_3(g) \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$
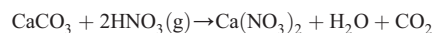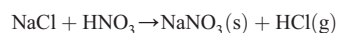
The reaction of HNO_3 with mineral dust is more efficient than that of SO_2 (Ooki and Uematsu, 2005). There was a significant relationship between equivalent concentrations of NO_3^- and nss-$Ca^{2+} + Na^+ - Cl^-$ without case c data (Fig. 9), indicating that most NO_3^- was associated with nss-Ca^{2+} and Na^+ in coarse particles when there was no longer a supply of NH_3 for equilibration with NH_4NO_3. These results are in good
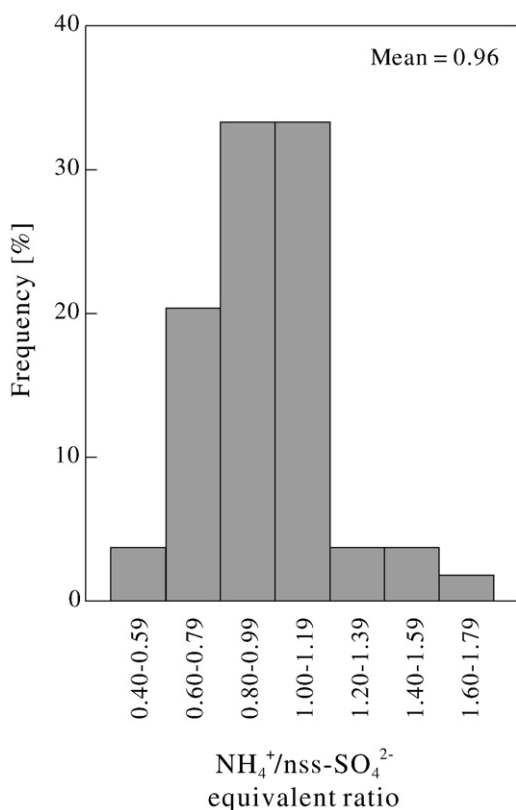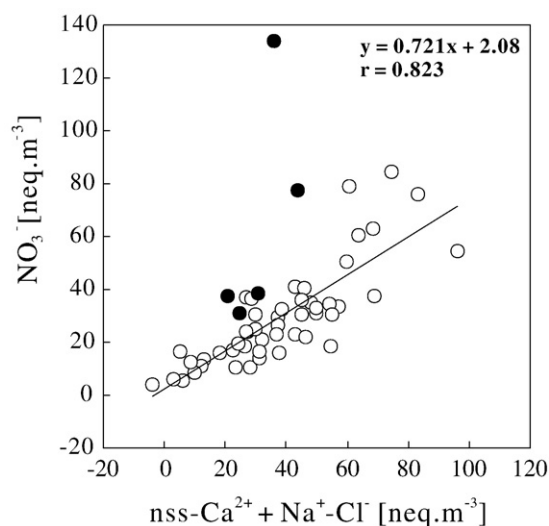
Fig. 9. Relationship between the concentrations of NO_3^- and nss-$Ca^{2+} + Na^+ - Cl^-$. Closed circles show the samples of case c in which there is complete neutralization of sulfate and excess NH_4^+ associated with other compounds (see text). Regression line was calculated without the samples of case c.

agreement with those for the remote islands where nitrate is in the form of $Ca(NO_3)_2$ (Shimohara et al., 2001; Matsumoto et al., 2003) and $NaNO_3$ (Shimohara et al., 2001) because there is an insufficient NH_3 concentration for NH_4NO_3 to form.

In case c, there is the possibility for NO_3^- to be associated partly with NH_4^+. If it is assumed the residual from the regression line obtained in Fig. 9 is for free nitrate associated with compounds other than nss-Ca^{2+} and Na^+, then the residual significantly correlates with the excess NH_4^+ calculated by subtracting NH_4^+ from nss-SO_4^{2-} (Fig. 10). These results indicate the formation of NH_4NO_3 for excess NH_4^+ (case c), although an excess of NH_4^+ scarcely occurred at the study site, unlike the case for urban areas.
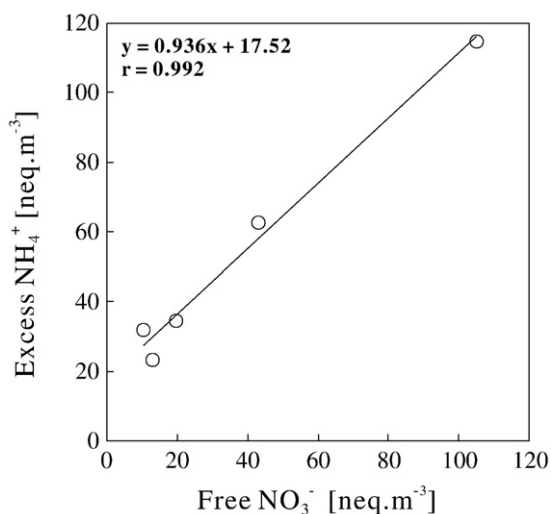

Fig. 10. Relationship between the concentrations of free NO_3^- as estimated from the regression line obtained from Fig. 9 and excess NH_4^+.

4. Summary and conclusions

Gaseous and particulate nitrogen and sulfate containing compounds were characterized at the inland suburban-forested site in northern Kyushu, western Japan from May 2006 to April 2007 using an annular denuder system 1) to evaluate the effects of regional emission of air pollutants and the long-range transport from East Asia on the ambient air quality of nitrogen and sulfur compounds and 2) to evaluate chemical forms of sulfate and nitrate particulates.

The annual mean concentration of HNO_3 at the study site was comparable to concentrations determined in urban areas in Japan and other countries. The diurnal variation of HNO_3 concentration, being higher in daytime and lower in nighttime, could be due to regional production of HNO_3 during daytime at the study site. The diurnal variation of wind direction suggests air pollutants emitted from the regional urban area were transported to the study site during the daytime and caused a higher HNO_3 concentration. The HNO_3 concentration was significantly higher in summer than in winter. However, the HNO_3 concentration in spring was comparable to that in summer in this study. Significant correlation between the F_n value and O_3 concentration suggests the concentration of HNO_3 in spring being comparable to that in summer was caused by the increased reaction of NO_2 with hydroxyl radicals (OH) derived from the photolysis of O_3 due to a higher concentration of O_3 in spring. It is suggested that the higher concentration of O_3 derived mainly from the long-range transport from East Asia enhanced regional HNO_3 production in spring.

The annual mean concentrations of SO_2 and nss-SO_4^{2-} at the study site were higher than concentrations determined in other urban areas and forested areas near urban areas in Japan and other countries. The SO_2 concentration was significantly higher in winter and spring than in summer. It is suggested that the long-range transport from East Asia in winter and spring caused the higher concentration of SO_2 at the study site. In contrast, there were no statistical differences in the nss-SO_4^{2-} concentrations among seasons, which is due to the higher relative humidity and higher temperature in summer enhancing the oxidation of SO_2 to SO_4^{2-}. The value of F_s being higher throughout the year at the study site (52.6%) than values determined in urban sites and there being no diurnal variation of F_s indicates the long-range transport of nss-SO_4^{2-} not only from East Asia but also from other areas including Japan.

The equivalent ratio of NH_4^+ and nss-SO_4^{2-} at the study site (0.96 ± 0.22) indicates that acidic sulfate is neutralized by NH_3, existing mainly as $(NH_4)_2SO_4$ in fine particles. It is suggested that NH_4NO_3 was not formed in most cases at the study site. A significant relationship between equivalent concentrations of NO_3^- and nss-$Ca^{2+} + Na^+ - Cl^-$ suggests nitrate is in the form of $Ca(NO_3)_2$ and $NaNO_3$ in coarse particles, which is similar to what has been found for sites where the NH_3 concentration is insufficient for NH_4NO_3 to form.

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