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Atmospheric Acidic Pollutants at Mt. Tsukuba, Japan, Determined Using a Portable Filter Pack Sampler

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We measured the concentrations of atmospheric acidic pollutants at Mt. Tsukuba using a newly developed portable filter pack sampler. The results were analyzed to characterize the distribution and origin of pollutants, and were compared with measurements from Tsukuba City and from other mountainous areas in Japan.

Increases in atmospheric acidic pollutants cause acid depositions that have adverse effects on forest ecosystems, as do ozone and water stress. In Japan, forest (or tree) decline has been reported around (or in) urban areas.[1] As well, recent deposition of excessive nitrogen into forest ecosystems has resulted in nitrogen saturation, causing serious environmental problems.[2] To elucidate these problems, information on the concentrations of atmospheric pollutants in mountainous areas is necessary. Although some long-term data (e.g. monthly averages) obtained by passive sampling have been available,[3–7] short-term data (e.g. daily averages) obtained usually by filter pack (FP) sampling are extremely limited, although these are more informative for monitoring and diagnosing forest health, because trees are often very sensitive to short-term high concentrations of pollutants. Therefore, we developed a battery-operated portable FP sampler to collect atmospheric acidic pollutants at mountainous sites without power supplies.[8] This FP method was applied to field measurements at Mt. Tsukuba.

Atmospheric concentrations of NO_x ($NO + NO_2$), SO_x ($SO_2 + SO_4^{2-}$), gaseous and particulate nitrate and chloride pollutants (T–NO_3 and T–Cl, respectively) were measured from November 2003 to March 2005 at Mt. Tsukuba (sites: top (T) and mid-slope (A–D)) and Tsukuba City (sites at the National Institute for Environmental Studies (NIES)), both of which are located in Tsukuba, Ibaraki, Japan (Fig. 1).

Daily mean concentrations of the atmospheric pollutants measured at Mt. Tsukuba are shown in Fig. 2, with those at

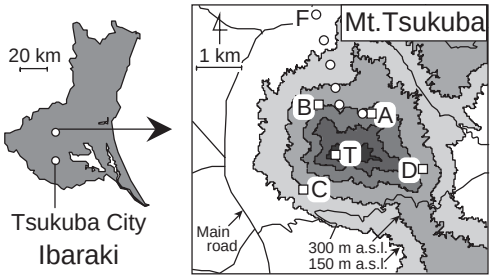

Fig. 1. Sampling sites at Mt. Tsukuba and Tsukuba City.

Tsukuba City. The concentration ranges (nmol m^{-3}) of NO_x, T–NO_3, SO_x, and T–Cl at Mt. Tsukuba were 113–440, 10–185, 26–481, and 11–69, respectively. Spatial variations among the top and mid-slope sites were small, and differences between sites were not significant ($p > 0.1$, Fisher's PLSD), although the diurnal (temporal) variations were relatively large.

NO_x concentrations at Mt. Tsukuba were low (mean $\pm$ standard deviation: 192 ± 101 nmol m^{-3}, $n = 17$), being about 20% of those in Tsukuba City (1284 ± 655 nmol m^{-3}, $n = 29$). Also, the ratio of NO_x concentrations at Mt. Tsukuba to those at Tsukuba City (by a chemiluminescence method,[9] see Experimental) on the same day were 0.20 ± 0.13 ($n = 17$), though there was no significant correlation between them ($p > 0.1$). NO_x concentration is affected by absorption by or emission from soil,[10] but the low NO_x concentrations on the mountain may have resulted mainly from the relatively long distance from the main source of pollutants (automobiles). In contrast, the traffic density near the sampling sites in Tsukuba City was at least 20000 vehicles per day,[11] contributing to the relatively high NO_x concentrations there. Additionally, the formation of a nocturnal inversion layer[12] may have decreased the NO_x concentrations at Mt. Tsukuba, by preventing NO_x, which would have been mainly produced by automobiles at the foot of the mountain, from being transported upward,[6] especially in winter. The vertical distributions of the pollutants along the northern slope (from sites F to A) during the night (16:00–6:00 JST) of November 17–18, 2004 are shown in Fig. 3, together with

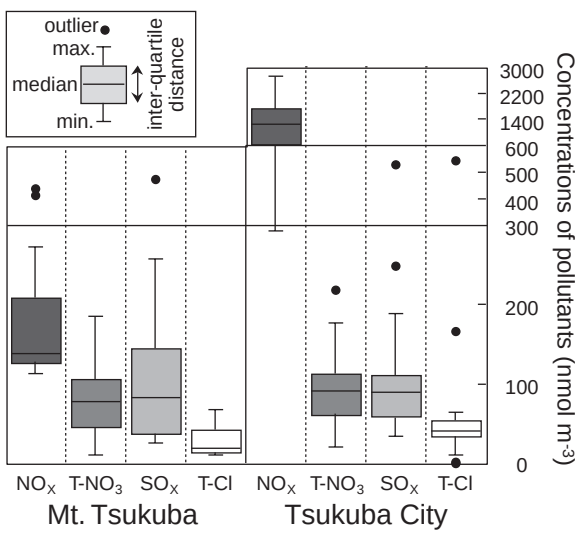

Fig. 2. Atmospheric concentrations of acidic pollutants at Mt. Tsukuba and Tsukuba City.

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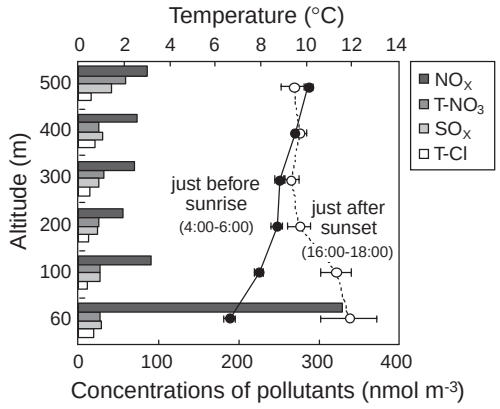

Fig. 3. Nighttime concentrations of atmospheric acidic pollutants (bar) and air temperature (circle) along the northern slope of Mt. Tsukuba.

those of temperature (similar distributions were obtained in other winter observations). NO_x concentration at 60 m was high, whereas those at above 100 m were uniformly low, and the formation of an inversion layer was observed from midnight to the just before sunrise.

Daily mean concentrations of T–NO_3 at Mt. Tsukuba (82 ± 54 nmol m^{-3}, $n = 13$) were almost the same as those in Tsukuba City (95 ± 49 nmol m^{-3}, $n = 29$) (Fig. 2), and thus T–NO_3/NO_x ratios were relatively high at Mt. Tsukuba, i.e., 0.42 ± 0.26 ($n = 13$), in contrast to 0.08 ± 0.04 ($n = 29$) at Tsukuba City. Nitrate is formed by the reaction of NO_2 with OH in daytime, and reactions of NO_3 with organics and N_2O_5 hydrolysis at nighttime.[13] Various atmospheric reactions and local meteorological conditions contribute to nitrate formation, and thus it is difficult to assume a dominant process related to the high T–NO_3 concentrations at Mt. Tsukuba. However, nitrate may have been transported from the urban areas in the Kanto district, especially in early winter.[14] The high T–NO_3 concentrations in mountains increase the nitrogen load to forest ecosystems, because the dry deposition velocity of T–NO_3 (especially HNO_3) to vegetation is faster than that of NO_x.[15] Although further investigation is necessary, increased NO_3^-–N loads at Mt. Tsukuba, due to the high atmospheric T–NO_3 concentrations, may have caused nitrogen saturation of the forest ecosystem and consequently the high NO_3^- concentrations in stream waters.[2]

SO_x concentrations at Mt. Tsukuba (119 ± 116 nmol m^{-3}, $n = 17$) were similar to those in Tsukuba City (109 ± 95 nmol m^{-3}, $n = 29$) (Fig. 2), and those at Mt. Tsukuba correlated well with SO_2 concentrations at Tsukuba City (by the UV fluorescence method,[9] $r = 0.893$, $p < 0.01$). Since there is no important local source of SO_x in the Tsukuba area, most of the SO_x may have originated from the same remote sources. A concentration of more than 200 nmol m^{-3} was observed three times, on February 20–21, March 16–17, and April 16–17, 2004. A back trajectory analysis using the CGER METEX[16] showed that the air masses at Mt. Tsukuba and Tsukuba City on these days had been transported from the volcano on Miyakejima Island (located 260 km SSW of Mt. Tsukuba). The air masses reaching the Tsukuba area on the other sampling days had not passed over Miyakejima Island. These results suggest that the exceptionally high SO_x concentrations resulted from volcanic gases discharged from Miyakejima Island.[3] Sea salt SO_4^{2-} is another factor affecting SO_x concentrations; however this contribution may have been minor, because the proportion of sea salt SO_4^{2-} to total SO_4^{2-} in the precipitation was generally less than 10% at Tsukuba City (based on our observations in 2003).

T–Cl concentrations at Mt. Tsukuba (28 ± 18 nmol m^{-3}, $n = 13$) were about 50% of those in Tsukuba City (60 ± 98 nmol m^{-3}, $n = 29$) (Fig. 2). T–Cl concentrations in Tsukuba City (and to a lesser extent at Mt. Tsukuba) may have been affected by anthropogenic emission, because a considerable amount of HCl is released from garbage incinerators in the Kanto district.[17] Also, the concentrations of T–Cl correlated well with those of SO_x ($r = 0.868$, $p < 0.01$, $n = 13$), suggesting the additional influence of volcanic gases.

Past data from Mt. Tsukuba and recent data from other mountainous areas in Japan are listed in Table 1.[3–7,18,19] Our data obtained at mountainous areas other than Mt. Tsukuba are also shown in the table. In comparison with the data obtained in 1976–1977,[18] NO_x and T–NO_3 concentrations at Mt. Tsukuba appear to have increased during the last several decades, in spite of the fact that the national averages of NO_x concentrations have remained almost constant since the 1980's.[20] This is probably due to the rapid increase of NO_x

Table 1. Mean Concentrations of Atmospheric Acidic Pollutants at Mountainous Areas in Japan

Site (Reference No.)	Method	Concentration/nmol m^{-3}							Period
		NO_x	NO_2	T–NO_3	SO_x	SO_2	SO_4^{2-}	T–Cl	
Mt. Tsukuba[a)]	FP[c)]	192	—[e)]	82	119	—	—	28	Nov. 2003–Mar. 2005
Mt. Tsukuba[18]	FP	—	73	25	62	9	52	—	Jun.–Jul. 1976–1977
Mt. Hiei[3]	Pa[d)]	386	226	—	—	98	—	—	Nov. 2000–Nov. 2002
Mt. Hiei[4]	Pa	—	292	—	—	146	—	—	Apr. 1996–Sep. 1998
Mt. Gokurakuji[5]	Pa	—	410	—	—	347	—	—	Jan.–Jun. 1995
Mt. Gokurakuji[6]	Pa	1005	656	—	—	—	—	—	Nov. 1994–May. 1995
Mt. Oyama[19]	FP	—	—	41	65	9	56	27	1995
Mt. Kushiishi[7]	Pa	37	24	—	—	5	—	—	Jun.–Oct., 2000
Mt. Hoji[a),b)]	FP	263	—	46	96	—	—	11	Sep. 2004
Mt. Kinsyo[a),b)]	FP	315	—	24	234	—	—	2	Aug. 2004
Mt. Tatsuware[a),b)]	FP	29	—	12	17	—	—	18	Sep. 2004
Mt. Sakurajima[a),b)]	FP	46	—	18	137	—	—	32	Aug. 2004

a) This study. b) $n = 3$. c) Filter Pack sampling. d) Passive sampling. e) Not measured.

emission with increases in the population and the number of automobiles around Mt. Tsukuba after the new city was developed (mainly post 1980's). Over a period of 27 years, the number of automobiles in Tsukuba area has increased 4.4 times, in contrast to the national average of 2.1.[21] SO_x concentrations also doubled, but our results were strongly affected by volcanic gases from Miyakejima Island. If the three exceptional cases exceeding 200 nmol m^{-3} are excluded, the recent mean SO_x concentration at Mt. Tsukuba was almost equivalent to that in 1976–1977.

The NO_x concentrations at Mt. Tsukuba were lower than those in mountains close to more urbanized cities or to roads with dense traffic (Mts. Hiei, Kinsyo, and Gokurakuji). However, they were higher than those in more rural areas (Mts. Kushiishi, Tatsuware, and Sakurajima). Therefore, the NO_x pollution at Mt. Tsukuba can be ranked at an intermediate level. Though SO_x concentrations at Mt. Tsukuba varied with the effect of volcanic gases from Miyakejima Island, the mean value was within the range of values observed in other areas, and the pollution was also at an intermediate level. The very high concentration of SO_x observed at Mt. Kinsyo was also due to a SO_2-rich air mass from Miyakejima Island. The high SO_x concentration at Mt. Sakurajima (this is also an active volcano) clearly resulted from volcanic gases discharged from the mountain itself. Although comparison of T–NO_3 and T–Cl was difficult because of the lack of data, especially from polluted areas, T–NO_3 concentrations at Mt. Tsukuba were the highest among the reported values.

Experimental

Concentrations of atmospheric acidic pollutants were measured by a method developed by the authors. The details have been reported previously;[8] therefore just an outline is described here. T–NO_3, SO_x, and T–Cl were collected on a Na_2CO_3 filter (quartz fiber), and NO_x on PTIO (2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl) + triethanolamine filters (cellulose, 6 piled sheets), respectively, by passing air sequentially through the filters at a flow rate of ca. 0.8 L min^{-1}, using a portable FP sampler. The pollutants trapped by the filters were extracted with water with or without H_2O_2, and the extracts were pre-cleaned (e.g. filtration, elimination of PTIO) and analyzed for anions (NO_3^-, SO_4^{2-}, Cl^-, and NO_2^-) by ion chromatography. Daily mean concentrations of pollutants in air (1 atm, 20 °C) were calculated from the amounts of pollutants analyzed and the total volumes of air sampled (mean: 1.188 m^3) The determination limits of NO_x, T–NO_3, SO_x, and T–Cl were about 40, 15, 10, and 20 nmol m^{-3} for 24-h sampling, respectively. Since simultaneous sampling by the FP method at Mt. Tsukuba and Tsukuba City was difficult (because of lack of personnel and samplers), NO_x concentrations by the chemiluminescence method (GLN-254, DKK) and SO_2 concentrations by the UV fluorescence method (GFS-32, DKK), both of which were obtained at the Air Monitoring Station of NIES,[9] were also used for comparison.

Mt. Tsukuba is an isolated mountain, located about 20 km north of Tsukuba City, about 70 km northeast of Tokyo and about 40 km west of the Pacific Ocean (Fig. 1). Sampling positions were about 1.5 m above the ground in open canopies, located at the top and mid-slope of the mountain (sites T and A–D). Sampling was conducted for 24 h at the selected 1–5 sites under fine weather conditions, and 17 times between November 2003 and March 2005 (once or twice a month; T–NO_3 and T–Cl were not measured at the first to fourth samplings). Nighttime (sunset to sunrise) sampling to investigate the effect of a nocturnal inversion layers on the vertical distribution of pollutants was conducted three times at six sites on the northern slope (from sites F to A) in winter, 2004. Sampling was also conducted at Tsukuba City (1–6 sites, 29 times) in the grounds of the NIES located near the center of the city. Apart from a garbage incinerator located about 10 km away from both site areas, there were no industrial activities producing polluting gases in the Tsukuba area. The number of automobiles in the Tsukuba area, which was expected to be a main NO_x source, was ca. 100000 in 2004.[21]

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