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Behavior and Origin of Atmospheric NO_2, SO_2, and O_3 in Mountains around the Kyoto Basin

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The behavior and origin of atmospheric NO_2, SO_2, and O_3 in mountains around the Kyoto basin were investigated by using passive samplers. Since these samplers are compact and need no batteries or pumps, they are appropriate for the measurement of atmospheric NO_2, SO_2, and O_3 at low-level concentrations in mountains or forests. The sampling sites were Mt. Hiei, Mt. Daimonji, and 7 other mountains around the Kyoto basin, and 4 clean sites (Seryu, Kuroda, Sasari, Ashu) located about 20—30 km north of the Kyoto basin. The concentrations of atmospheric NO_2, SO_2, and O_3 in mountains on three sides of the Kyoto basin were almost the same at the same altitude in the same season. The source of atmospheric NO_2 in mountains around the Kyoto basin may be anthropogenic emission from automobiles or industrial areas, and NO_2 concentration at clean sites far away from the Kyoto basin may become lower due to the diffusion of NO_2. O_3 concentration was higher as the altitude increased. Atmospheric O_3 at mountains around the Kyoto basin has its origin in both stratospheric input and O_3 production by photochemical reactions.

In recent years, "acid rain" has received great attention as a global environmental problem because of the effect of acidic deposition within various ecosystems.[1,2] The decline of the number of Japanese cedar and pine trees has frequently been reported in Japan.[3—5] For this reason, since 1991, the environmental effect of acid deposition on the acidity and chemical properties of soils has been investigated using soil samples collected from Mt. Hiei and neighboring mountains in Kyoto City. The average soil pH (H_2O) of the A_0 layer (humus layer) and the lower layer for samples from 15 mountains were 3.96 and 4.26, respectively. Based on the acidity and chemical properties of soils, it is suggested that the acid-buffering capacity of the soils of the mountains on three sides of the Kyoto basin will decrease considerably in the near future, as indicated by soil pH as well as exchangeable Ca and Mg and exchangeable Al and sulfate concentrations in the soils.[6] Furthermore, the chemical properties of soils in these mountains were different depending on the altitude.[7]

It is important to elucidate the roles of air pollutants in influencing the biogeochemical cycles in mountains or forests. However, as almost all of the continuous monitoring stations are set up in urban areas, it is impossible to estimate the concentrations of air pollutants in mountains or forests. Passive samplers are suitable for simultaneous and multi-point measurements of air pollutants, since they are structurally simple and need no batteries or pumps. In our previous studies,[8,9] a simple analysis of atmospheric NO_2, SO_2, and O_3 in mountains or forests by passive samplers was developed and applied to the spatial analysis of atmospheric NO_2, SO_2, and O_3 along the slope of Mt. Hiei in Kyoto City. In this study, the behavior and origin of atmospheric NO_2, SO_2, and O_3 in mountains around the Kyoto basin were investigated by means of these passive samplers.

Experimental

Sampling Sites in Mountains around the Kyoto Basin. The sampling sites were Mt. Hiei and 8 other mountains around the Kyoto basin and 4 other sites (Seryu (altitude, 700 m), Kuroda (altitude, 310 m), Sasari (altitude, 730 m) and Ashu (altitude, 400 m)) located about 20—30 km north of the Kyoto basin (Fig. 1). Sampling of air pollutants was carried out in 13 locations at Mt. Hiei from the Hiei summit cable-car station (altitude, 700 m) to

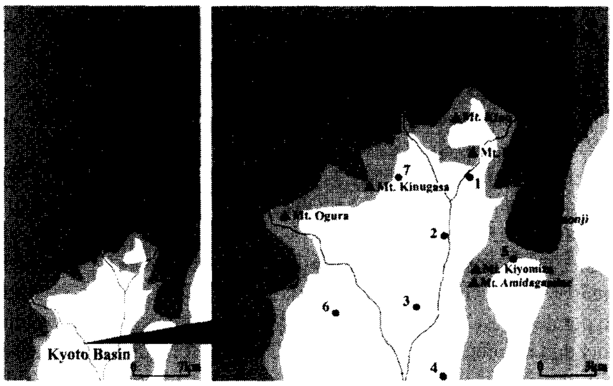

Fig. 1. Sampling sites of atmospheric NO_2, SO_2, and O_3 in mountains around the Kyoto basin, 4 sites located about 20—30 km north from the Kyoto basin, and public monitoring sites of Kyoto City. 1: Sakyo-ku, 2: Nakagyo-ku (Kyoto City Hall), 3: Minami-ku, 4: Fushimi-ku, 5: Yamashina-ku, 6: Nishikyo-ku, 7: Kita-ku.

the foot (altitude, 170 m). The eight mountains around the Kyoto basin were: Mt. Ogura (altitudes: 60, 175, 300 m), Mt. Kinugasa (altitudes: 90, 190 m), Mt. Higashi (altitudes: 80, 185m), Mt. Kino (altitudes: 60, 160 m), Mt. Uryu (altitudes: 80, 185m), Mt. Daimonji (altitudes: 110, 210, 340 m), Mt. Kiyomizu (altitude, 220 m), and Mt. Amidagamine (altitudes: 160, 196 m). Air pollutants were collected at each altitude. Measurements by passive samplers were carried out at 34 points. Measurements at Mt. Hiei began in May 1995, and further measurements at other sampling sites began in May 1997. Seven public monitoring sites in Kyoto City are also shown in Fig. 1.

Measurement Procedures for Atmospheric NO_2, SO_2, and O_3 by the Passive Samplers. Atmospheric NO_2, SO_2, and O_3 in mountains were determined by passive samplers according to our previous studies.[8,9] A Yanagisawa-type sampler, which consists of an impregnated filter with triethanolamine and is commercially available (Toyo Roshi, Filter Badge NO_2), was used for the determination of atmospheric NO_2. After the sampler had been exposed for 30 d, the absorbent filter was taken out and put in a beaker, and 100 ml of Saltzman reagent was added to it. After the reagent had been standing for 1 h, the absorbance was measured at 545 nm spectrophotometrically.

The amount of absorbed NO_2 through a cross-sectional area A (cm^2) during exposure of t (s) becomes M (mol):

$$M = K_{OG}At(1/RT)f \times 10^{-9}. \qquad (1)$$

Here, K_{OG} is the overall mass-transfer coefficient and f is the NO_2 concentration in ppb; R and T are the gas constant and temperature, respectively. By setting $K_{OG} = 0.14$ cm s^{-1} under 20 °C, 60% of relative humidity, and 2.0 m s^{-1} of wind velocity, the amount of absorbed NO_2 (M) is described as follows:

$$M = 4.97 \times 10^{-9} f. \qquad (2)$$

Accordingly, atmospheric NO_2 concentration (f) can be calculated from the amount of absorbed NO_2 (M) obtained from the calibration curve by the Saltzman method.

The SO_2 sampler, which was made up of an absorbent filter containing sodium carbonate, was made by us as described in our previous studies.[8,9] After the SO_2 sampler had been exposed for 30 d, the absorbent filter was taken out and put in a 30-ml polyethylene container containing 15 ml of distilled water. Absorbed SO_2 was readily oxidized to SO_4^{2-} with the addition of 0.3 ml of 30% H_2O_2 solution. These sample solutions were stored in a refrigerator and determined by ion chromatography (IC) within 2 weeks. A Shimadzu Model HIC-6A ion chromatograph was used. 500 µl of sample was injected through a cation-exchange cartridge (Tosoh TOYOPAK IC-SP S). A guard column (Shim Pack IC-GA3) and an analytical column (Shim Pack IC-A3) were used at 40 °C. 3.2-mM Bistris-8 mM p-hydroxy benzoic acid was used as an eluent with a flow rate of 1.5 ml min^{-1}.

The O_3 sampler developed by Harvard University,[10—12] which consists of collecting filters coated with a solution including sodium and potassium salts of nitrite and carbonate, glycerol, methanol, and water and is commercially available (Ogawa Co., Kobe, Japan), was used for the determination of atmospheric O_3 in mountains. This sampler was set by using a protective cup which acts as both a windscreen and a rain cover. After the sampler had been exposed for 30 d, two absorbent filters were transferred to a polyethylene bottle containing 5 ml of distilled water and sonicated for 15 min. These sample extracts were stored in a refrigerator and analyzed by ion chromatography (IC) within 1 week. Twenty µl of sample was injected through a cation-exchange cartridge (Tosoh TOYOPAK IC-SP S). The other conditions for the measurement of nitrate concentration were the same as those for that of sulfate concentration stated above.

The average O_3 concentration, C (ppb), during exposure of t (min) can be calculated by the following equation:

$$C = MV(W_{O_3}/W_{NO_3^-})/SK(W_{O_3})t, \qquad (3)$$

where M is the net nitrate concentration in ppm, V is the extraction volume, and W_{O_3} and $W_{NO_3^-}$ are the molecular weights of ozone and nitrate ion, respectively. K is 0.0409 µmol/ppb m^{-3} under 25 °C and 1 atm. Outdoors, under a wind shield, the collection rate (S) of the passive sampler was 24.5 cm^3/min^{-1},[10] whereas it was 17.8 cm^3 min^{-1} indoors.[12]

Results and Discussion

Variation of Atmospheric NO_2 and SO_2 Concentrations at Mountains in Kyoto City. Figure 2 shows the monthly changes in the concentrations of NO_2 at Mt. Daimonji (altitude, 340 m), Mt. Hiei (altitude, 370 m), Mt. Ogura (altitude, 310 m), Kuroda, and Ashu from May 1997 to July 1999. Mt. Daimonji, Mt. Hiei, and Mt. Ogura are located around the Kyoto basin, while Kuroda and Ashu are located about 20—30km north of the Kyoto basin. The concentration range of atmospheric NO_2 at Mt. Daimonji was 5.1—12.9 ppb, while that at Mt. Hiei and Mt. Ogura was 2.9—8.2 ppb. The NO_2 concentrations at Kuroda and Ashu were 1.2—2.3 and 0.5—1.2 ppb, respectively, which was only one-tenth of those at mountains around the Kyoto basin. A seasonal variation of atmospheric NO_2 similar to that at Mt. Hiei, which shows a winter maximum and a summer minimum, was clearly observed at almost all mountains around the Kyoto basin, but it was not clear at 4 sites far away from the Kyoto basin. The higher NO_2 concentration in winter may be attributed to the formation of a temperature-inversion

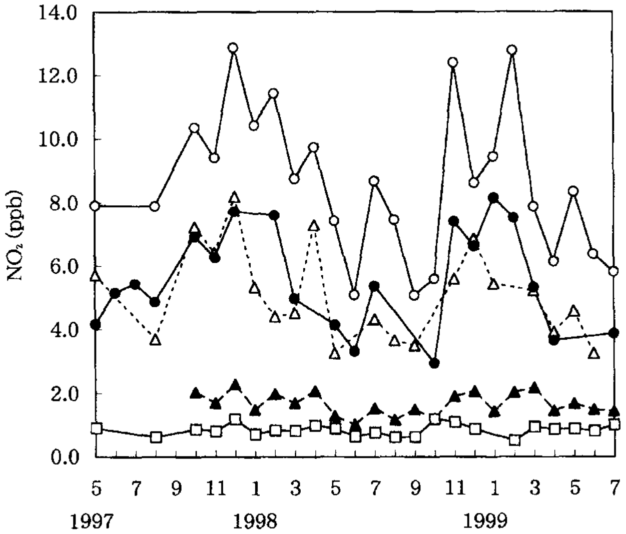

Fig. 2. Seasonal changes in the concentration of NO_2 at Mt. Daimonji, Mt. Hiei, Mt. Ogura, Kuroda, and Ashu from May 1997 to July 1999. ○: Mt. Daimonji (altitude: 340 m), ●: Mt. Hiei (370 m), △: Mt. Ogura (300 m), ▲: Kuroda, □: Ashu

layer. The lower NO_2 concentration in summer may be due to the destruction of NO_2 by a photochemical reaction with OH radicals because summer solar radiation is generally the strongest.[13] Three-dimensional graphs of atmospheric NO_2 concentration at mountains in Kyoto (z) in relation to the distance (x) from the city hall ($x = 0$) and altitude (y) in August 1998, December 1998, and April 1999 are shown in Fig. 3. The NO_2 concentrations at Mt. Amidagamine and Mt. Kiyomizu located east-southeast of the city hall, were higher compared with those at mountains located north of the city hall. The high NO_2 concentration may result from the anthropogenic emission from automobiles or neighboring industrial areas because of a major highway running at the side of these mountains and industrial areas located south of them. Several black circles at 0—10 km north of the city hall indicate mountains around the Kyoto basin. White circles indicate the sampling points at Mt. Hiei. It was found that the NO_2 concentrations at mountains around the Kyoto basin were almost the same at the same altitude in the same season. The mean NO_2 concentrations at mountains around the Kyoto basin were 5.1 ppb in August and 8.6 ppb in December, respectively. The NO_2 concentration decreased gradually with an increase of altitude and was the largest at an altitude of around 300 m. These results may be attributed to both the formation of a temperature-inversion layer at an altitude of around 300 m[9,14] and a regional inflow of pollutants. The NO_2 concentrations at 4 sites (Seryu, Sasari, Kuroda, and Ashu) located 20—30 km north of the Kyoto basin were very low. These results suggest that the source of atmospheric NO_2 in the mountains of Kyoto City may be anthropogenic emission from automobiles or industrial areas and NO_2 concentration at sampling locations far away from anthropogenic emissions may become lower due to the diffusion of NO_2.

The monthly changes in the concentrations of SO_2 at Mt. Daimonji, Mt. Hiei, Mt. Ogura, Kuroda, and Ashu from May 1997 to July 1999 are shown in Fig. 4. The concentration range of atmospheric SO_2 at Mt. Daimonji was 2.0—4.1 ppb, while that at Mt. Hiei and Mt. Ogura was 1.5—3.8 ppb. The SO_2 concentrations at Kuroda and Ashu were 1.1—2.4 and 1.2—2.5 ppb, respectively. The background of SO_2 concentration and the mean SO_2 concentration in Japan were reported to be 1—2 and 3—3.2 ppb, respectively.[15] The SO_2 concentrations at Kuroda and Ashu are consistent with the background of SO_2 concentration in Japan. The seasonal variations of atmospheric SO_2 at mountains around the Kyoto basin did not show a regular pattern, but those at suburban areas such as Kuroda and Ashu exhibited a clearly regular pattern with the highest level in spring. Uno et al.[16] have reported that the intermittent transport of pollutants strongly

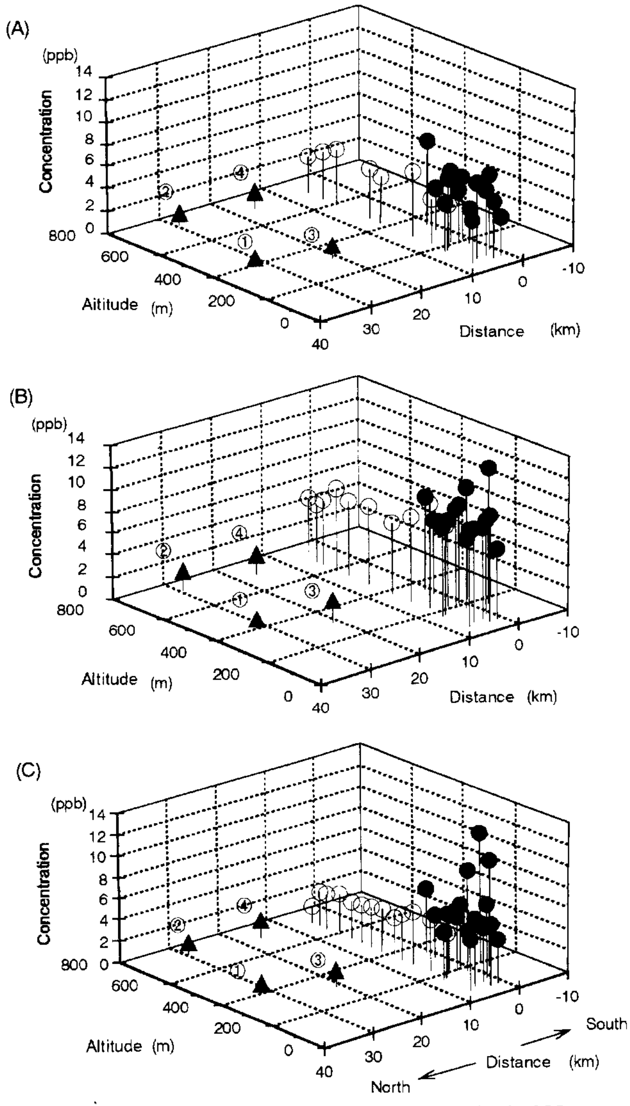

Fig. 3. Three-dimensional graphs of atmospheric NO_2 at mountains in Kyoto. (A) August 1998, (B) December 1998, (C) April 1999. ●: mountains around the Kyoto basin, ○: Mt. Hiei, ▲: ① Ashu, ② Sasari, ③ Kuroda, ④ Seryu.

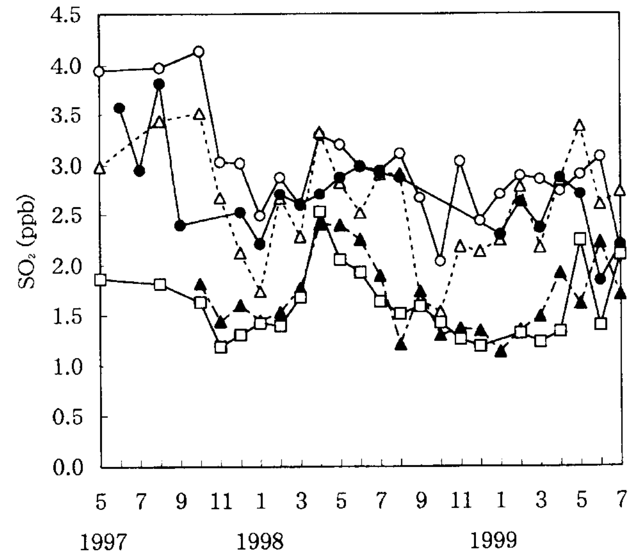

Fig. 4. Seasonal changes in the concentration of SO_2 at Mt. Daimonji, Mt. Hiei, Mt. Ogura, Kuroda, and Ashu from May 1997 to July 1999. ○: Mt. Daimonji (altitude: 340 m), ●: Mt. Hiei (340 m), △: Mt. Ogura (300 m), ▲: Kuroda, □: Ashu.

correlated with the passage of synoptic scale high/low pressure system in spring. The highest SO_2 concentrations every spring at suburban areas in Kyoto may be due to the long-range transport of SO_2 from the continental region or the emission from Mt. Sakurajima (Kagoshima Pref.). Three-dimensional graphs of atmospheric SO_2 concentration at mountains in Kyoto (z) in relation to the distance (x) from the city hall ($x = 0$) and altitude (y) in August 1998, December 1998, and April 1999 are shown in Fig. 5. The SO_2 concentrations at mountains around the Kyoto basin were slightly higher than those at 4 sites (Seryu, Sasari, Kuroda, and Ashu) located 20—30 km north of the Kyoto basin, indicating that the SO_2 concentrations at mountains around the Kyoto basin are somewhat affected by the anthropogenic emissions from neighboring industrial areas.

Variation of Atmospheric O_3 Concentration at Mountains around the Kyoto Basin. The seasonal changes of atmospheric O_3 at Mt. Daimonji, Mt. Hiei, Mt. Ogura, Kuroda, and Ashu from May 1997 to July 1999 are shown in Fig. 6. The concentration range of atmospheric O_3 at Mt. Daimonji was 17.5—41.8 ppb, while that at Mt. Hiei and Mt. Ogura was 17.2—37.0 ppb. The O_3 concentrations at Kuroda and Ashu were 11.4—30.8 and 8.8—32.2 ppb, respectively. The variation of O_3 exhibited a regular pattern with a maximum in spring and a minimum in winter at suburban areas such as Kuroda and Ashu, but another peak in autumn was also observed at mountains around the Kyoto basin. The spring maximum of O_3 in Japan has been suggested to be due to stratospheric intrusion.[16—18] Sunwoo et al. have reported that the seasonal cycle of surface ozone at Amami and Iriomote exhibited bimodal peaks in autumn as well as spring and ascribed the autumn peak to the outflow of an ozone-rich continental air mass in this season.[19] However, since an autumn peak of O_3 was not observed at Kuroda or Ashu, it is difficult to say that the cause of the autumn peak at mountains around the Kyoto basin is due to the outflow of an O_3-rich continental air mass. The cause may be O_3 production by a photochemical reaction with anthropogenic NO_x. Three-dimensional graphs of atmospheric O_3 concentration at mountains in Kyoto (z) in relation to the distance (x) from the city hall ($x = 0$) and altitude (y) in August 1998, December 1998, and April 1999 are shown in Fig. 7. The regional variation of atmospheric O_3 was smaller than that of atmospheric NO_2. Moreover, the O_3 concentration was higher with an increase of altitude, which may be due to stratospheric intrusion and surface destruction.[21] It has been reported that tropospheric O_3 has its origin in both stratospheric input and in-situ production by a photochemical reaction in the atmosphere polluted by anthropogenic sources.[21—23]

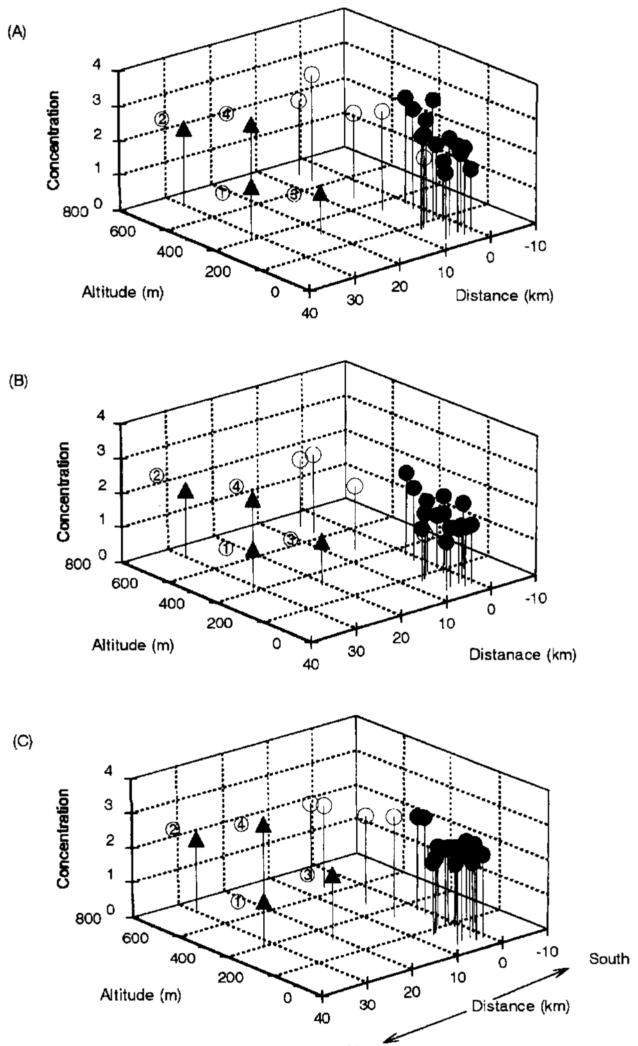

Fig. 5. Three-dimensional graphs of atmospheric SO_2 at mountains in Kyoto. (A) August 1998, (B) December 1998, (C) April 1999. ●: mountains around the Kyoto basin, ○: Mt. Hiei, ▲: ① Ashu, ② Sasari, ③ Kuroda, ④ Seryu.

Origin of Atmospheric NO_2 and O_3 at Mountains around the Kyoto Basin. Monthly-averaged daily changes

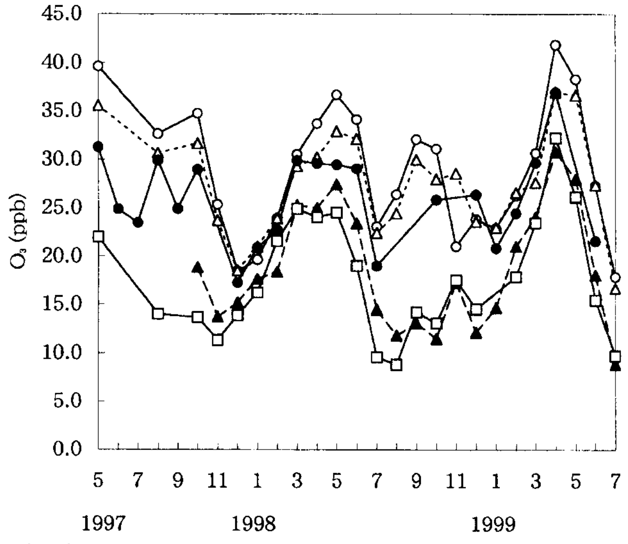

Fig. 6. Seasonal changes in the concentration of O_3 at Mt. Daimonji, Mt. Hiei, Mt. Ogura, Kuroda, and Ashu from May 1997 to July 1999. ○: Mt. Daimonji (altitude: 340 m), ●: Mt. Hiei (370 m), △: Mt. Ogura (300 m), ▲: Kuroda, □: Ashu.

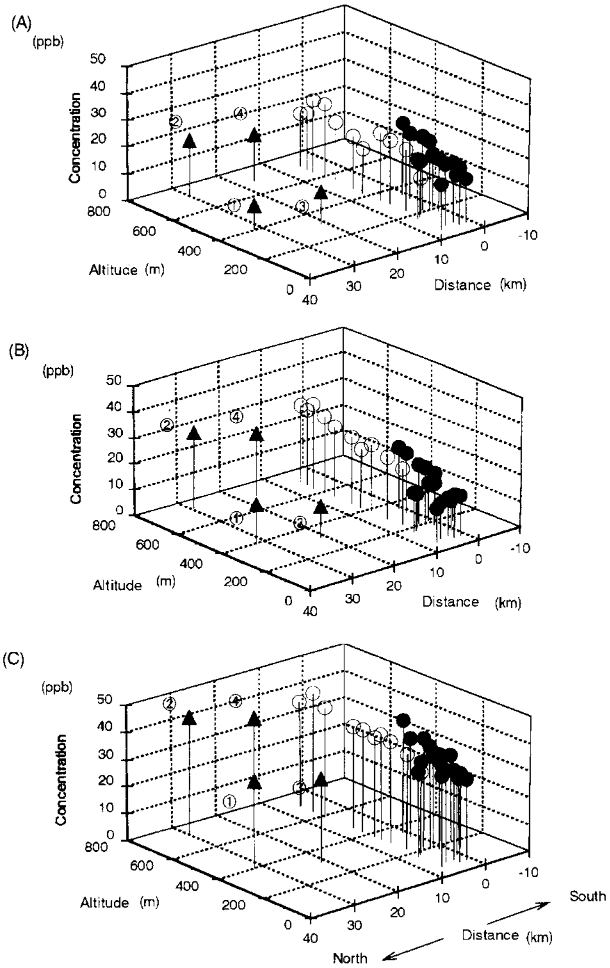

Fig. 7. Three-dimensional graphs of atmospheric O_3 at mountains in Kyoto. (A) August 1998, (B) December 1998, (C) April 1999. ● : mountains around the Kyoto basin, ○: Mt. Hiei, ▲: ① Ashu, ② Sasari, ③ Kuroda, ④ Seryu.

of atmospheric NO_2 and oxidants concentrations at the public monitoring site 1 (Sakyo-ku), located near Mt. Hiei, in August 1998, December 1998, and April 1999 are shown in Fig. 8. The atmospheric NO_2 concentration was high from 8:00 to 11:00 and from 18:00 to 22:00 due to the anthropogenic emission from automobiles. The peak of oxidants occurred at 14:00—15:00 and was higher in the following order: December 1998 < April 1999 < August 1998. This may be attributed to the strong photochemical activities resulting from intense solar radiation. The diurnal variation of atmospheric O_3 in the experimental farm of the Kyoto Institute of Technology, which is located near Mt. Ogura, exhibited a maximum at 12:00—14:00, becoming higher with winds from the south or southwest direction. These results suggest that the high concentration of oxidants every afternoon may result from not only O_3 production by a photochemical reaction, but also O_3 transport from industrial areas located south of Kyoto City. The concentrations of oxidants in August 1998 and December 1998 decreased rapidly during the night due to O_3 scavenging by NOx, but that in April 1999 did not decrease so much. Then, the concentrations of oxidants at 6:00 in August 1998 and December 1998 were 14 and 9 ppb, while that at in April 1999 was 36 ppb, which was close to the peak concentration in December 1998. The higher concentration of oxidants in spring could be explained by the combination of less destruction at night and larger injection from stratosphere than those in other seasons.[24—26] The seasonal changes in the concentrations of NO_2 and oxidants at seven public monitoring sites from April 1997 to March 1998 are shown in Fig. 9. The NO_2 concentrations at monitoring sites 1 and 3 (Minami-ku) were 14—24 and 22—36 ppb, respectively, which was 2—3 times higher than those at mountains around the Kyoto basin. A seasonal variation of atmospheric NO_2 similar to those at mountains around the Kyoto basin, which shows a winter maximum and a summer minimum, was observed at all monitoring sites in Kyoto City. The higher NO_2 concentration in winter may be attributed to the formation of a temperature-inversion layer, because the formation of a temperature-inversion layer in winter and summer was 5—9 d and 0—2 d in a month, respectively. The concentration ranges of oxidants at monitoring sites 1 and 3 were 20—44 and 15—40 ppb, which were similar to those at mountains around the Kyoto basin such as Mt. Daimonji, Mt. Hiei and Mt. Ogura. Seasonal trends were also similar to those at mountains around the Kyoto basin.

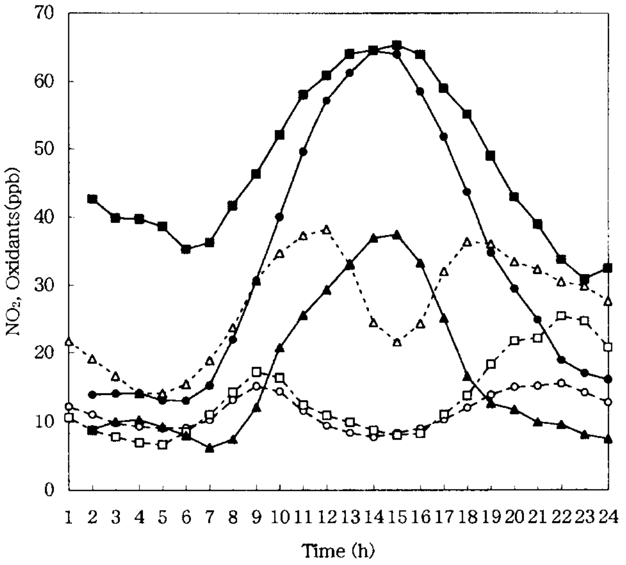

Fig. 8. Monthly-averaged daily changes of atmospheric NO_2 and oxidants concentrations at the public monitoring site 1 (Sakyo-ku) in August 1998 (○, ●), December 1998 (△, ▲), and April 1999 (□, ■). NO_2: ○, △, □, Oxidants: ●, ▲, ■.

As atmospheric O_3 concentration varies with altitude,[9] it was compared with that at mountains with similar altitudes. The ratios (y/x) of atmospheric O_3 and NO_2 concentrations at several locations at altitudes of 300—400 m (y) compared to those at Mt. Daimonji (altitude, 340 m) (x) were calculated. Figures 10(A) and 10(B) show the seasonal changes in the ratios of atmospheric O_3 and NO_2, respectively. The ratios of atmospheric O_3 at Mt. Hiei and Mt. Ogura were almost 1.0, and their seasonal changes were small. How-

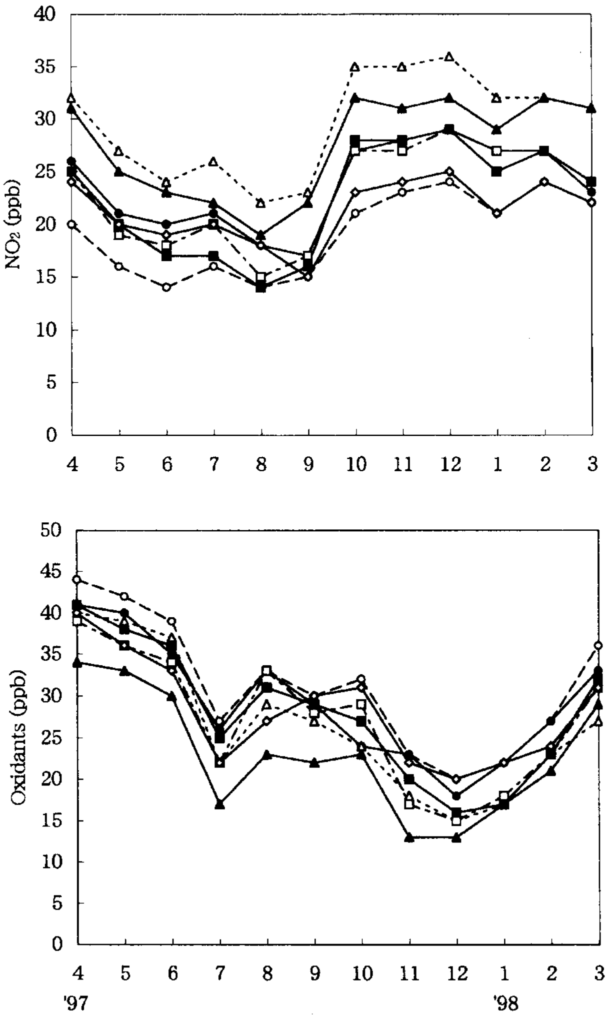

Fig. 9. Seasonal changes in the concentrations of atmospheric NO_2 and oxidants at seven public monitoring sites from April 1997 to March 1998. ○: Sakyo-ku, ●: Nakagyo-ku (Kyoto City Hall), △: Minami-ku, ▲: Fushimi-ku, □: Yamashina-ku, ■: Nishikyo-ku, ◇: Kita-ku.

ever, the seasonal changes in the ratios of atmospheric O_3 at suburban areas such as Kuroda and Ashu were large. The ratios were about 0.4—0.5 in autumn and about 0.8—0.9 in winter. On the other hand, the ratios of atmospheric NO_2 were smaller as distance from Mt. Daimonji increased, and the seasonal changes of the ratios did not show a regular pattern even at suburban areas such as Kuroda and Ashu. Similarly, the ratios (y/x) of atmospheric O_3 and NO_2 concentrations at several locations at altitudes of about 700 m (y) compared to those at Mt. Daimonji (altitude, 340 m) (x) were calculated. Figures 11(A) and 11(B) show the seasonal changes in the ratios of atmospheric O_3 and NO_2, respectively. The ratios of atmospheric O_3 at Mt. Hiei, Seryu, and Sasari were 1.2—1.4 in winter and 0.7—0.8 in autumn. The ratios of atmospheric O_3 at an altitude of about 700 m were about 0.3 larger in each season than those of atmospheric O_3 at Kuroda and Ashu. The difference may result from the difference of altitude. The ratios of atmospheric NO_2 were smaller as the distance from Mt. Daimonji increased,

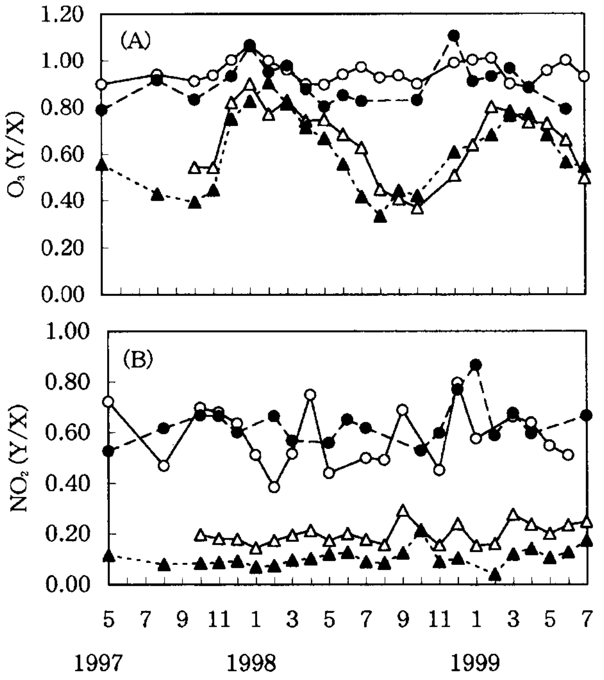

Fig. 10. Seasonal changes in the ratios of atmospheric O_3 (A) and NO_2 (B) concentrations at several locations at altitudes of 300—400 m (y) compared to those at Mt. Daimonji (altitude; 340 m). ○ : Mt. Hiei (340 m), ●: Mt. Ogura (300 m), △: Kuroda (310 m), ▲ : Ashu (400 m).

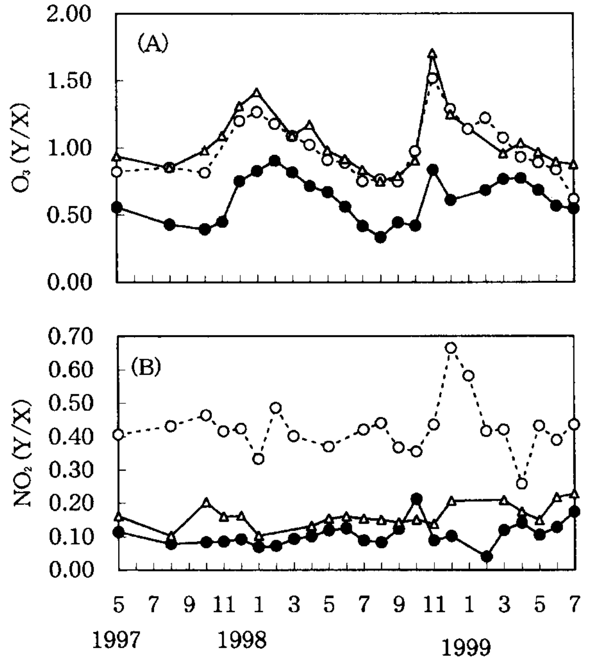

Fig. 11. Seasonal changes in the ratios of atmospheric O_3 (A) and NO_2 (B) concentrations at several locations at altitudes of about 700 m (y) compared to those at Mt. Daimonji (altitude; 340 m). ○: Mt. Hiei (700 m), ●: Seryu (700 m), △: Sasari (730 m).

and their seasonal changes were small even at suburban areas. The seasonal variations of O_3 at these mountains, with a spring maximum and a winter minimum, were similar to those at four clean sites located north of the Kyoto basin. The high O_3 concentration in spring was observed when the relative humidity at Mt. Hiei became lower with a decrease of altitude, which may be due to stratospheric intrusion. The O_3 concentration at Mt. Daimonji around the Kyoto basin was higher than that at Ashu by 2—2.5 times in the period from summer to autumn and 1.2—1.5 times from winter to spring. The difference may be attributed to O_3 production resulting from anthropogenic NO_x emission. The contribution of photochemical O_3 production in tropospheric O_3 at mountains around the Kyoto basin in the period from summer to autumn could be estimated to be larger than that from winter to spring. Uno et al.[16] have reported that the origin of tropospheric O_3 in spring is mainly stratospheric input and 10—30% of photochemical O_3 production. From our results, atmospheric O_3 at mountains around the Kyoto basin may have its origin in both stratospheric input and O_3 production by a photochemical reaction. However, since the estimate of both contributions in tropospheric O_3 at mountains around the Kyoto basin is difficult, further study is needed.

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References

1 B. I. Chevone and S. N. Linzon, *Environ. Pollut.*, **50**, 87 (1988).

2 S. E. Lindberg, M. Bredemeier, D. A. Schafer, and L. Qi, *Atmos. Environ.*, **24**, 2207 (1990).

3 M. Nashimoto and K. Takahashi, *Shinrin Ritti* [in Japanese], **32**, 70 (1990).

4 K. Takahashi, M. Nashimoto, and H. Ueta, *Environ. Sci.*, **4**, 51 (1991).

5 M. Nashimoto, K. Takahashi, and S. Ashihara, *Environ. Sci.*, **6**, 121 (1993).

6 T. Yamada, M. Ohno, M. Sato, and E. Yamada, *Environ. Sci.*, **9**, 211 (1996).

7 T. Yamada, M. Ohno, and E. Yamada, "Conference of the Environmental Science Society," 1995, Abstr., p. 59.

8 E. Yamada, D. Yoshida, L.-C. Hu, and T. Yamada, *Bunseki Kagaku*, **12**, 1083 (1996).

9 E. Yamada, M. Kimura, K. Tomozawa, and Y. Fuse, *Environ. Sci. Technol.*, **33**, 4141 (1999).

10 P. Koutrakis, J. M. Wolfson, A. Bunyaviroch, S. E. Froehlich, K. Hirano, and J. D. Mulik, *Anal. Chem.*, **65**, 209 (1993).

11 L.-J. S. Liu, M. P. Olson, G. A. Allen, P. Koutrakis, W. F. McDonnel, and T. R. Gerrity, *Environ. Sci. Technol.*, **28**, 915 (1994).

12 L.-J. S. Liu, P. Koutrakis, J. Leech, and I. Broder, *J. Air Waste Manage Assoc.*, **45**, 223 (1995).

13 P. J. Crutzen, J. Lelieveld, and C. Bruhl, in "Environmental Oxidants," ed by J. O. Nriagu and M. S. Simmons, John Wiley & Sons, New York (1994) pp. 63—93.

14 Kyotoshi Eiseikyoku, "Kyotoshi no Kankyo [Health Bureau of Kyoto City; Environment in Kyoto City; in Japanese]," 1994.

15 S. Fujita, *Environ. Sci.*, **9**, 185 (1996).

16 I. Uno, K. Murano, and S. Wakamatsu, *J. Jpn. Soc. Atmos. Environ.*, **33**, 164 (1998).

17 T. Ogawa and A. Miyata, *J. Meteorol. Soc. Jpn.*, **63**, 937 (1985).

18 H. Tsuruta, K. Shinya, T. Mizoguchi, and T. Ogawa, in "Ozone in the Atmosphere," ed by R. D. Bojikov and P. Fabian, A. Deepak, Hampton, Va. (1989).

19 Y. Sunwoo, G. R. Cavmichael, and H. Ueda, *Atmos. Environ.*, **28**, 25 (1994).

20 T. Mizoguchi, S. Mitsumoto, and M. Nishikawa, *Environ. Sci.*, **2**, 87 (1989).

21 J. Fishman, S. Solomon, and P. J. Cruzen, *Tellus*, **31**, 432 (1979)

22 P. T. Cruzen, *Ann. Rev. Earth Planet Sci.*, **7**, 443 (1979).

23 J. A. Logan, *J. Geophys. Res.*, **90**, 10463 (1985).

24 H. B. Singh, W. Viezee, W. B. Johnson, and F. L. Ludwig, *J. Air. Pollut. Control Assoc.*, **30**, 1009 (1980).

25 J. J. Yienger, A. A. Klonecki, H. Levy, II, W. J. Moxim, and G. R. Carmichael, *J. Geophys. Res.*, **104**, 3655 (1999).

26 P. Pochanart, J. Hirokawa, Y. Kajii, and H. Akimoto, *J. Geophys. Res.*, **104**, 3621 (1999).