Bull. Chem. Soc. Jpn., 77, 497–503 (2004)

Effects of an Eruption on Miyake Island on the Behavior of Air Pollutants and Chemical Components of Rainwater in Kyoto

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Continuous measurements of air pollutants (NO_x, SO_2, O_3) by passive samplers and chemical components of rainwater in Kyoto were made from 1996 to 2002. An eruption on Miyake Island and urban climate changes were found to greatly affect the seasonal changes of air pollutants and chemical components of rainwater in 2000 and 2001. Several peaks of NO_2 concentrations at mountains around the Kyoto basin occurred in the spring and summer of 2000 and 2001. The higher NO_2 concentration in the summer of 2000 and 2001 may be attributed to the formation of a temperature-inversion layer. Atmospheric SO_2 concentrations became abruptly higher in September 2000, and the concentration range of atmospheric SO_2 in mountains around the Kyoto basin was 1.0–7.9 ppb from September 2000 to July 2001, which was about two-times higher than that until 1999. These results suggest that a large quantity of SO_2 discharge by the eruption on Miyake Island may have affected the increase of atmospheric SO_2 concentrations in Kyoto. The O_3 concentrations in the summer of 2000 and 2001 were higher than that until 1999. The cause may be O_3 production by a photochemical reaction with an increase of anthropogenic NO_x in the warm months after 2000. The concentration of gaseous H_2O_2 was very low when the SO_2 content was high in September, 2000, and in June and July, 2001, which may have been due to a large quantity of SO_2 discharge that occurred as a result of the eruption on Miyake Island. These results indicate that gaseous H_2O_2 may largely determine the formation of aerosol sulfate in the warm months. Thus, the increase of anthropogenic or natural SO_2 emission may significantly affect the increase of $SO_4{}^{2-}$ concentration in rainwater.

Acid rain has received great attention as a global environmental problem because of the effect of acidic deposition within various ecosystems.[1,2] A decline 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 values of the 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 the soil pH as well as the 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] Therefore, the role of air pollutants, such as atmospheric NO_2, SO_2, and O_3, on the biogeochemical cycles in mountains or forests, was investigated using passive samplers.[8–10] Diurnal and seasonal variations of H_2O_2 concentrations in the atmosphere and rainwater have been measured in Kyoto since 1998. The factors affecting the formation of atmospheric H_2O_2 were analyzed, and the effects of H_2O_2 on the oxidation of SO_2 in rainwater were evaluated.[11]

It is important to investigate the long-term behavior of air pollutants (NO_x, SO_2, O_3) and the chemical components of rainwater in order to elucidate the role of acidic deposition on the biogeochemical cycles in mountains or forests. After the investigations, continuous measurements of air pollutants (NO_2, SO_2, O_3) using passive samplers in mountains around the Kyoto basin and of chemical components of rainwater in Kyoto City were made from 1996 to 2002. Furthermore, since October 1999, additional measurements were carried out at Miyadzu, Kayadani, Yasaka, and Kumihama, located in the northern part of Kyoto Prefecture, for the analysis of long-range transport from the continental region. In this study, measurements of NO were also obtained using passive samplers. Here, we report on continuous measurements of air pollutants (NO_x, SO_2, O_3) and chemical components of rainwater in Kyoto from 1996 to 2002 and discuss the effects of the eruption on Miyake Island and urban climate changes on the seasonal changes of air pollutants and chemical components of rainwater in 2000 and 2001.

Experimental

Sampling Sites. The sampling sites were at Mt. Hiei and five other mountains around the Kyoto basin and Kuroda (altitude: 310 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 the base (altitude: 170 m). The five mountains around the Kyoto basin were Mt. Ogura (altitude: 60, 175, 300 m), Mt. Kinugasa (altitude: 90, 190 m), Mt. Higashi (altitude: 80, 185 m), Mt. Daimonji (altitude:

Published on the web March 12, 2004; DOI 10.1246/bcsj.77.497

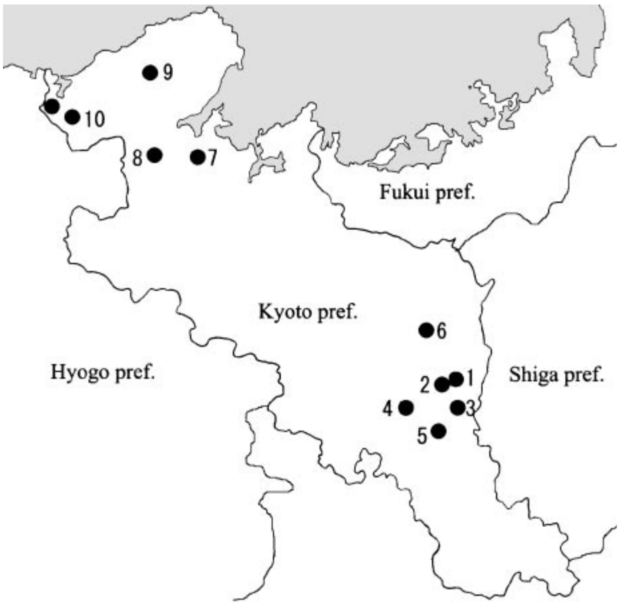

Fig. 1. Sampling sites of atmospheric NO_2, SO_2, and O_3 in Kyoto. 1: Mt. Hiei, 2: Mt. Higashi, 3: Mt. Daimonji, 4: Mt. Ogura, 5: Mt. Kiyomizu, 6: Kuroda, 7: Miyadzu, 8: Kayadani, 9: Yasaka, 10: Kumihama.

110, 210, 340 m), and Mt. Kiyomizu (altitude: 220 m). Air pollutants were collected at each altitude described below. Measurements by passive samplers were carried out at 25 points. Measurements at Mt. Hiei began in May 1995, and further measurements at other sampling sites began in May 1997. Furthermore, since October 1999, measurements have been carried out from sampling stations at Miyadzu, Kayadani, Yasaka, and Kumihama, located in the northern part of Kyoto Prefecture (Fig. 1). Since January 1996, rainwater samples have been collected on the roof of the chemistry building (10 m height above ground surface) at the Kyoto Institute of Technology (Sakyo-ku, Kyoto). The data from a public monitoring site (Takano, Sakyo-ku) in Kyoto City was used.

Measurement Procedures for Atmospheric NO_x, SO_2, and O_3 Using Passive Samplers. Atmospheric NO_2, SO_2, and O_3 in the mountains were determined using passive samplers according to our previous studies.[8–10] 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 days, 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 left standing for 1 h, the absorbance was measured spectrophotometrically at 545 nm. A Hirano-type sampler, which is commercially available from the Ogawa Co., Kobe, Japan[12,13] and consists of two kinds of impregnated filters with triethanolamine for collecting atmospheric NO_2 and with triethanolamine and 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO) for collecting both atmospheric NO and NO_2, was used for the determination of atmospheric NO and NO_2. This sampler was set by using a protective cup, which acted as both a windscreen and a rain cover. After the sampler had been exposed for 30 days, two absorbent filters were transferred to each glass test tube containing 8 mL of distilled water, and the test tube was occasionally shaken for 30 min before cooling at 2–6 °C. After the addition of ascorbic acid for the reduction of PTIO to the tube containing an impregnated filter with triethanolamine and PTIO, 2 mL of Saltzman reagent was added. After the reagent had been standing for 1 h, the absorbance was spectrophotometrically measured at 545 nm.

The SO_2 sampler, which was made up of an absorbent filter containing sodium carbonate, was made as described in previous papers.[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. Five hundred μL of the 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.

The O_3 sampler developed by Harvard University,[14–16] 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 the 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 the sample was injected through a cation-exchange cartridge (Tosoh TOYOPAK IC-SP S). The other conditions for the measurement of the nitrate concentration were the same as those for the sulfate concentration stated above.

Measurement Procedures for Chemical Components in Rainwater. Rainwater samples (wet deposition only) were collected per 1 mm and during one event using two Rain-Go-Round Models (Horiba Co., Ltd.). A sample of rainwater, which was filtered through a cellulose acetate filter (Advantec DISMIC-13cp, pore size 0.2 μm) and stored in a refrigerator, was determined within 2 d. The concentrations of anions (SO_4^{2-}, NO_3^-, Cl^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) in rainwater were determined by ion chromatography. A Shimadzu Model HIC-6A ion chromatograph and a Shimadzu Model PIA-1000 ion chromatograph were used. Atmospheric H_2O_2 and aqueous H_2O_2 in rainwater were collected and determined according to our previous studies.[11]

Results and Discussion

Variation of Atmospheric NO_x (NO_2, NO) in Kyoto. The seasonal changes in the concentrations of atmospheric NO_2 in the mountains around the Kyoto basin and Kuroda located about 20–30 km north of the Kyoto basin were investigated from 1997 to 2002. Figure 2 shows the seasonal changes in the concentrations of NO_2 at the public monitoring site (Takano, Sakyo-ku) and Mt. Hiei (altitude: 170 m, 300–400 m, 700 m) from 1997 to 2002. At Mt. Hiei, the NO_2 concentrations at an altitude of 300–400 m and 700 m were 2.4–11.4 ppb and 1.4–7.3 ppb, respectively, while that at the public monitoring site (Takano, Sakyo-ku) was 8.9–26.0 ppb, which was three times that at Mt Hiei. The concentration range of atmospheric NO_2 at Mt. Daimonji (altitude: 340 m) was 4.2–13.8 ppb, while those at Mt. Ogura (altitude: 310 m) and Kuroda were 2.2–8.2 ppb and 1.0–2.6 ppb, respectively. Mt. Daimonji and Mt. Ogura are located around the Kyoto basin, while Kuroda is located

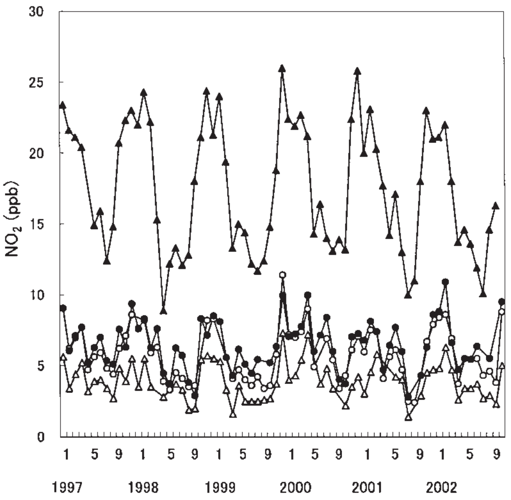

Fig. 2. Seasonal changes in the concentration of NO_2 at Mt. Hiei and a public monitoring site (Sakyo-ku, Kyoto City) from January 1997 to November 2002. Mt. Hiei: altitude ○: 170 m, ●: 300–400 m, △: 700 m, ▲: public monitoring site (Sakyo-ku).

about 20–30 km north of 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 Kuroda, far away from the Kyoto basin. The higher NO_2 concentration in winter may be attributed to the formation of a temperature-inversion layer, and the lower NO_2 concentration in summer may be due to the destruction of NO_2 by a photochemical reaction with OH radicals because solar radiation is generally the strongest.[10,17] The concentrations and variations of atmospheric NO_2 at these sites in Kyoto from 1997 to 2002 were almost the same as those from 1997 to 1999.[10] However, several peaks of NO_2 concentrations at mountains around the Kyoto basin occurred in the spring and summer of 2000 and 2001. The higher NO_2 concentration in the summer of 2000 and 2001 may be attributed to the formation of a temperature-inversion layer because the formation of a temperature-inversion layer in the summers of 2000 and 2001 was 7–9 d, which is larger than that in the summers of other years, 0–2 d.

The seasonal changes in the concentrations of NO at the public monitoring site (Takano) and Mt. Hiei (altitude: 170 m, 300–400 m, 700 m) from November 2000 to December 2002 are shown in Fig. 3. At Mt. Hiei, the NO concentrations at an altitude of 460 m and 700 m were 2.1–8.4 ppb and 1.6–6.2 ppb, respectively, while that at the public monitoring site (Takano) was 2.8–16.1 ppb, which was five-times that at Mt. Hiei in the winter and almost the same as that at Mt. Hiei in April and August. The small difference in the NO concentrations between Takano and Mt. Hiei may be attributed to the rapid reaction of NO to NO_2 with the oxidation of O_3 because the atmospheric O_3 concentrations in these periods were high. A seasonal variation of atmospheric NO, similar to that of NO_2, shows a winter maximum and a summer minimum.

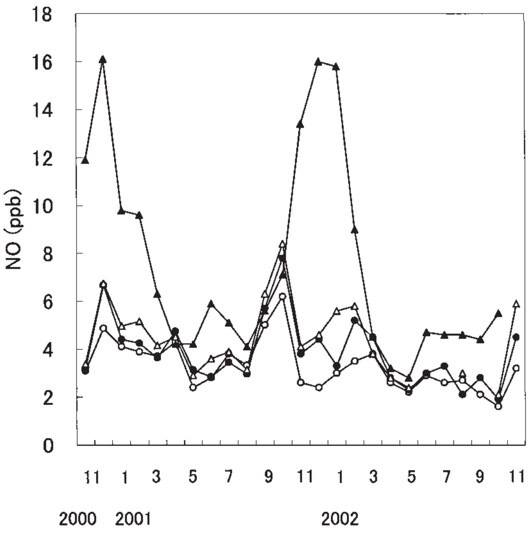

Fig. 3. Seasonal changes in the concentration of NO at Mt. Hiei and a public monitoring site (Sakyo-ku, Kyoto City) from November 2000 to November 2002. Mt. Hiei: altitude ○: 170 m, ●: 300–400 m, △: 700 m, ▲: public monitoring site (Sakyo-ku).

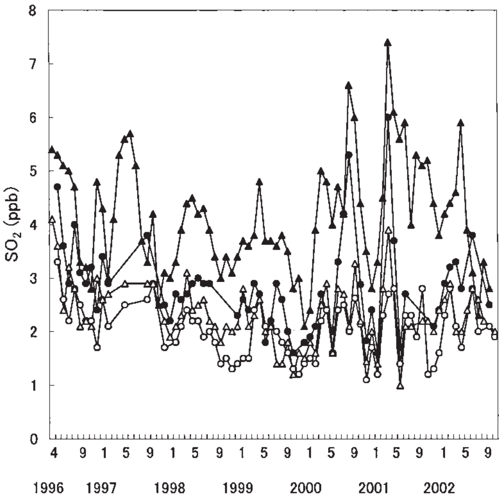

Fig. 4. Seasonal changes in the concentration of SO_2 at Mt. Hiei and a public monitoring site (Sakyo-ku, Kyoto City) from April 1996 to November 2002. Mt. Hiei: altitude ○: 170 m, ●: 300–400 m, △: 700 m, ▲: public monitoring site (Sakyo-ku).

Variations in Atmospheric SO_2 Concentrations in Kyoto and the Effects of the Eruption on Miyake Island. The seasonal changes in the concentrations of SO_2 at the public monitoring site (Takano, Sakyo-ku) and Mt. Hiei (altitude: 170 m, 300–400 m, 700 m) from April 1996 to 2002 are shown in Fig. 4. The seasonal changes in the concentrations of SO_2 at Mt. Daimonji (altitude: 340 m), Mt. Ogura (altitude: 310 m), and Kuroda from 1998 to 2002 were also analyzed. The concentration range of atmospheric SO_2 at mountains around Kyoto City was 1.0–4.0 ppb until 1999, and their seasonal variations, which were small, showed a regular pattern with the highest level in the spring. Uno et al. have reported that the intermittent transport of pollutants strongly correlated with the passage of the synoptic scale high/low pressure system in the spring.[18] However, atmospheric SO_2 concentrations abruptly became higher on September 2000, and the concentration range of atmospheric SO_2 at the mountains around the Kyoto basin was 1.0–7.9 ppb from September 2000 to July 2001, which was about two times higher than that until 1999. After August 2001, the atmospheric SO_2 concentrations were below 4.0 ppb at the mountains around the Kyoto basin. The seasonal changes that occurred since October 1999 in the atmospheric SO_2 concentrations were further investigated at Miyadzu, Kayadani, Yasaka, and Kumihama, which are located in the northern part of Kyoto Prefecture. The concentration range of atmospheric SO_2 at these sites was 1.2–7.4 ppb during measurement, and a rapid increase in September 2002 and large variations from September 2000 to July 2001 were also observed, which were the same as those in the mountains around the Kyoto basin. However, a regular pattern with the highest level in the spring could not be clearly observed because of an abrupt increase of atmospheric SO_2.

Time variations of the atmospheric SO_2 concentrations at the public monitoring site (Takano, Sakyo-ku, Kyoto) and SO_2 flux from Miyake Island are shown in Fig. 5. Miyake Island is a volcanic island about 10 km across, located at 150 km south of Tokyo. Volcanic activity in 2000 started in late June and a large eruption occurred on August 18 with plume height over 12 km. Since then volcanic gases has been released intensively. The average SO_2 emission per day in 2000 and 2001 were 21000 t/d and 42000 t/d, respectively.[19–21] The average SO_2 emission rate of Miyake Island largely exceeded 8000 t/d of Popocatepetl volcano in Mexico, which was the world maximum release until now. And, it is reported[20] that the total amount of SO_2 emission from Miyake Island so far was 15 million tons from September 2000 to mid May 2002. Atmospheric SO_2 concentrations in Kyoto were especially high from September to November in 2000 and from April to July in 2001 (Fig. 5). During this period, the rate for the wind of the south-southeast from the east was 0.3–0.5 and SO_2 emission from Miyake Island was large. On September 13, 2000, the highest concentration of SO_2 was observed in Kinki, about 400–500 km far from volcano.[22] In Kyoto, atmosphere SO_2 concentration at 19:00–21:00 on September 13 was very high, which were 103–151 ppb. A backward trajectory analysis suggested that the volcanic emissions were transported from Miyake Island.[23] The atmospheric SO_2 concentrations in Kyoto were also high on April 2001, which were 130–136 ppb at 19:00–21:00 on April 8 and 202 ppb at 15:00 on April 19. The simulations of volcanic gas diffusion from Miyake Island on April 2001, which were calculated by the System for Prediction of Environmental Emergency Dose (SPEEDI)[24] developed in Japan Atomic Energy Research Institute, suggested that the high concentration of SO_2 in Kyoto may be largely due to the emissions from Miyake Island.

These results suggest that a large quantity of SO_2 discharge by the eruption on Miyake Island and weather conditions may affect the increase of atmospheric SO_2 concentrations in Kyoto.

Variation of Atmospheric O_3 Concentrations in Kyoto. The seasonal changes in the concentrations of atmospheric O_3 in the mountains around the Kyoto basin and Kuroda located about 20–30 km north of the Kyoto basin were investigated from 1997 to 2002. The seasonal changes in the concentrations of O_3 at the public monitoring site (Takano, Sakyo-ku) and Mt. Hiei (altitude: 170 m, 300–400 m, 700 m) from April 1997 to 2002 are shown in Fig. 6. 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, but another peak in autumn was also observed at the mountains around the Kyoto basin. The spring maximum of O_3 in Japan has been suggested to be due to stratospheric intrusion.[18,25,26] Sunwoo et al. 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.[27] However, since an autumn peak of O_3 was not observed at Kuroda, it is difficult to say that the cause of the autumn peak in the mountains around the Kyoto basin is due to the outflow of an O_3-rich continental air mass. Further-

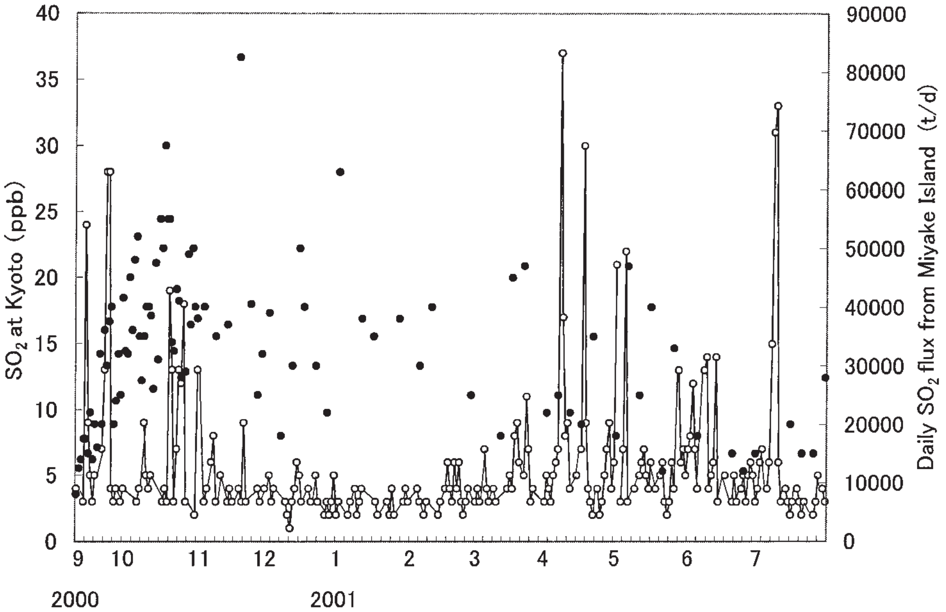

Fig. 5. Time variations of the atmospheric SO_2 concentrations at the public monitoring site (○; Takano, Sakyo-ku, Kyoto) and SO_2 flux from Miyake Island (●).

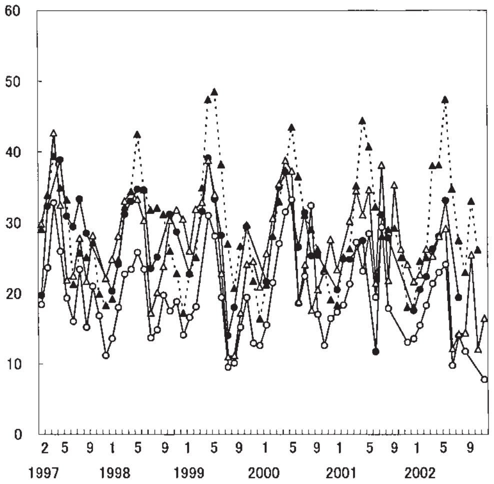

Fig. 6. Seasonal changes in the concentration of O_3 at Mt. Hiei and a public monitoring site (Sakyo-ku, Kyoto City) from January 1997 to November 2002. Mt. Hiei: altitude ○: 170 m, ●: 300–400 m, △: 700 m, ▲: public monitoring site (Sakyo-ku).

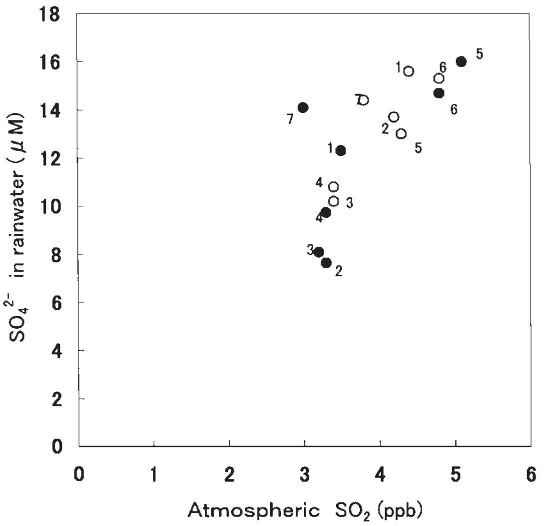

Fig. 7. Relationship between the concentrations of SO_4^{2-} in rainwater and atmospheric SO_2 from 1996 to 2002 in Kyoto. ○: Yearly average, ●: Average of September to December; 1: 1996, 2: 1997, 3: 1998, 4: 1999, 5: 2000, 6: 2001, 7: 2002.

more, another peak of the O_3 concentration in the summer was observed after 2000. At the public monitoring site (Takano) during 1999 and 2001, the monthly means of O_3 concentrations at 14:00 and 5:00 exhibited a maximum in April–August and in April, respectively. Then, the differences in the monthly means of O_3 concentrations between 14:00 and 5:00 were high in the summer (June–August), and those in the summer of 2000 and 2001 were higher than that in 1999. The cause may be O_3 production by a photochemical reaction with an increase of anthropogenic NO_x after 2000. Moreover, the O_3 concentration was higher with an increase in the altitude, which may be due to a stratospheric intrusion and surface destruction.[28] It has been reported that tropospheric O_3 has its origin in both the stratospheric input and in situ production by a photochemical reaction in the atmosphere polluted by anthropogenic sources.[28–30] The seasonal changes in the concentrations of atmospheric O_3 since October 1999 at Miyadzu, Kayadani, Yasaka, and Kumihama, which are located in the northern part of Kyoto Prefecture, were investigated. The concentration range of atmospheric O_3 at these sites was 5.9–50.0 ppb during measurements, the values being similar to those in Kyoto City.

Effects of Air Pollutants on the Chemical Components of Rainwater The concentrations of chemical components and pH in rainwater have been measured since 1994 in Kyoto. The pH values ranged from 3.30 to 6.60, with a mean of 4.50 during 1994–1999. However, the pH values of rain samples from September to December 2000, which ranged from 3.3 to 4.8, were much lower than those in the same seasons of other years. After April 2001, the pH values were in the range of 4.1 to 6.2.

The SO_4^{2-} wet deposition fluxes of one event in Kyoto during 1994–2002 ranged from 3.7 to 2070 μmol m^{-2} event^{-1}. The wet depositions of SO_4^{2-} in 1999, 2000, and 2001 were 17.0, 17.5, and 18.8 mmol m^{-2} y^{-1}, respectively. The averages of atmospheric SO_2 and volume-weighted averages of the SO_4^{2-} concentration in rainwater of Kyoto during 1996–2002 were calculated. The averages of atmospheric SO_2 were 4.3 ppb in 2000 and 5.1 ppb from September to December 2000, which were larger than those, 3.4 ppb in 1998 and 3.4 ppb in 1999. The volume-weighted averages of the SO_4^{2-} concentration in rainwater were 13.0 μM in 2000 and 16.1 μM from September to December 2000, which were larger than those, 10.2 μM in 1998 and 10.8 μM in 1999. These values were also large in 2001, but became smaller in 2002. These results suggest that a large quantity of SO_2 discharge by the eruption on Miyake Island in June 2000 may have affected the increase of atmospheric SO_2 concentrations from September 2000 to July 2001 in Kyoto, and, furthermore, the increase of SO_4^{2-} concentration in rainwater. The relationship between the volume-weighted averages of the SO_4^{2-} concentration in rainwater and the averages of atmospheric SO_2 concentrations during 1996–2002 is shown in Fig. 7. A positive relation was obtained. These results strongly suggest that the atmospheric SO_2 content significantly affects the SO_4^{2-} concentration in rainwater. The averages of atmospheric NO_2 and the volume-weighted averages of the NO_3^- concentration in rainwater of Kyoto during 1996–2002 were also calculated. However, no relation was obtained between the averages of atmospheric NO_2 and the volume-weighted averages of the NO_3^- concentration in rainwater. This case was entirely different from the case of atmospheric SO_2 and SO_4^{2-} in rainwater. The difference may depend on the solubility difference of gaseous SO_2 and NO_2. The solubility for gaseous SO_2 (11.3 g in 100 g of water at 20 °C) is relatively larger than that for NO_2 (0.006 g in 100 g of water at 20 °C).

Hydrogen peroxide (H_2O_2) and O_3 in air are considered to be the most important oxidants of SO_2 in the atmosphere, and H_2O_2 is the dominant oxidant for SO_2 in rainwater[31,32] at pHs less than 5. Moreover, the toxic effect of O_3 on trees is thought to be one of the causes for the recent dieback of forests in eastern North America and central Europe.[31,33] H_2O_2 is also a toxic compound for plant cells and might be another reagent responsible for forest decline.[34] However, few studies concern-

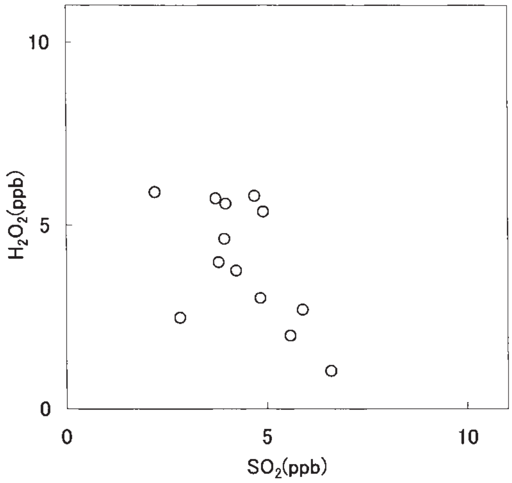

Fig. 8. Relationship between the concentrations of atmospheric H_2O_2 and SO_2 from 1999 to 2002.

ing the long-term behavior of H_2O_2 in the atmosphere and rainwater have been carried out in Japan.[35] In a previous study,[11] the concentrations of H_2O_2 in the atmosphere and rainwater were measured in Kyoto, and the factors affecting the formation of atmospheric H_2O_2 were analyzed. Moreover, the effect of H_2O_2 on the oxidation of SO_2 in rainwater was evaluated.

The relationship between atmospheric SO_2 (monthly average) and gaseous H_2O_2 at 14:00 (fine day) in the summer during 1999–2002 is shown in Fig. 8. Gaseous H_2O_2 was found to be inversely correlated with atmospheric SO_2. Atmospheric H_2O_2 showed high values of 4.0–5.7 ppb during June and September 1999, while the atmospheric SO_2 concentrations were 3.6–3.8 ppb. The concentrations of gaseous H_2O_2, 1.0–2.7 ppb during September 2000 and June and July 2001 were very low when the SO_2 contents, 5.6–6.6 ppb were high, which may be due to a large quantity of SO_2 discharge by the eruption on Miyake Island. These results indicate that gaseous H_2O_2 may be rapidly consumed by atmospheric SO_2, and largely determine the formation of aerosol sulfate during the warm months.

From these results, it is assumed that H_2O_2 could be a dominant oxidant of SO_2 during the warm season and that atmospheric SO_2 may be easily converted to aerosol sulfate, which is consistent with previous results.[11] Accordingly, the increase of anthropogenic or natural SO_2 emission may significantly affect the increase of the SO_4^{2-} concentration in rainwater.

We would like to express our sincere appreciation to Prof. Toshiharu Furusawa and Dr. Masatoshi Ichida for kindly providing continuous monitoring data from the experimental farms at the Kyoto Institute of Technology. We would like to thank the Health Bureau and the Research Center for Health and Pollution of Kyoto City for providing the continuous monitoring data. We would like to thank the high school teachers of Kyoto Prefecture, Mr. Yasunori Yamamoto, Mr. Yosiaki Oohiro, Mr. Muneo Mashima, and Mr. Hikohito Mori for their help in sampling air pollutants at Miyadzu, Kayadani, Yasaka, and Kumihama. We also thank the students of our laboratory and Mr. Tetsuji Okada for their help in sampling air pollutants in the mountains. A part of the present study was supported by the Nippon Life Insurance Foundation.

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, "Abstracts of Papers, 1995," Conference of the Environmental Science Society (1995), p. 59.

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

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

10 E. Yamada, M. Kimura, K. Tomozawa, and Y. Fuse, *Bull. Chem. Soc. Jpn.*, **73**, 1291 (2000).

11 E. Yamada, K. Tomozawa, Y. Nakanishi, and Y. Fuse, *Bull. Chem. Soc. Jpn.*, **75**, 1385 (2002).

12 K. Hirano, H. Maeda, and K. Matsuda, *Kankyo to Sokuteigijyutu* [in Japanese], **12**, 32 (1985).

13 K. Hirano, H. Maeda, and K. Matsuda, *Papers of Yokohama Environmental Research Institute* [in Japanese], 128 (1997).

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

15 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).

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

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

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

19 K. Kazahaya, *Sigenkankyotaisaku* [in Japanese], **37**, 33 (2001).

20 K. Kazahaya, H. Shinohara, K. Uto, M. Odai, H. Mori, Y. Nakabori, H. Iino, and J. Hirabayashi, "Abstracts of Papers, 2002 [in Japanese]," Conference of the Japan Society of Atmospheric Environment (2002), pp. 120–123.

21 National Institute of Advanced Industrial Science and Technology, Geological Survey of Japan web site: updated on Sep. 2003, http://www.aist.go.jp/GSJ.

22 R. Matsumoto, M. Karaushi, S. Yonemoti, and K. Murano, "Abstracts of Papers, 2001 [in Japanese]," Conference of the Japan Society of Atmospheric Environment (2001), p. 273.

23 I. Noguchi, M. Akiyama, and T. Ebana, *Report of Hokkaido Institute of Environmental Sciences* [in Japanese], **29**, 40 (2002).

24 Japan Atomic Energy Research Institute web site, Miyake Island volcanic gas diffusion simulation by System for Prediction of Environmental Emergency Dose Information (SPEEDI): updated on Sep. 2003, http://des.tokai.jaeri.go.jp/incoming/miyake.html.

25 T. Ogawa and A. Miyata, *J. Meteorol. Soc. Jpn.*, **63**, 937

(1985).

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

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

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

29 P. T. Cruzen, *Annu. Rev. Earth Planet. Sci.*, **7**, 443 (1979).

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

31 H. Sakugawa and I. R. Kaplan, *J. Geophys. Res.*, **94**, 12957 (1989).

32 T. Ibusuki, M. Ohsawa, and K. Takeuchi, *Atmos. Environ.*, **24A**, 1325 (1990).

33 S. B. McLaughlin, *J. Air Pollut. Control Assoc.*, **35**, 512 (1985).

34 G. Masuch, A. Kettrup, R. K. A. M. Mallant, and J. Slanina, *J. Environ. Anal. Chem.*, **27**, 183 (1986).

35 T. Yamashita, H. Sakugawa, and K. Fujiwara, *Nippon Kagaku Kaishi* [in Japanese], **1994**, 1127.