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Behavior of Hydrogen Peroxide in the Atmosphere and Rainwater in Kyoto, and Its Effect on the Oxidation of SO_2 in Rainwater

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The diurnal and seasonal variations of hydrogen peroxide (H_2O_2) concentrations in the atmosphere and rainwater were measured in Kyoto since 1998, and the factors affecting the formation of atmospheric H_2O_2 were analyzed. The concentration of atmospheric H_2O_2 was larger in the daytime than at night, the difference being small in the winter and large during the spring and summer. The seasonal variation of atmospheric H_2O_2 in Kyoto, 0.09–5.8 ppbv, showed a summer maximum and a winter minimum. The concentration of atmospheric H_2O_2 correlated the most with the solar radiation, UV radiation and temperature, while it was inversely correlated with the relative humidity. Atmospheric H_2O_2 increased rapidly above ca. 20 °C. The formation of atmospheric H_2O_2 may be mainly due to a photochemical reaction. The H_2O_2 concentration in rainwater had a high level of 1.2–65.1 μM ($1\ \mathrm{M} = 1\ \mathrm{mol\ dm^{-3}}$) in the summer, while maintaining a low level of less than 0.01 μM in the winter. Gaseous H_2O_2 may be rapidly removed from the atmosphere by wet deposition and aqueous H_2O_2 in rain may originate mostly from gas-phase H_2O_2. The wet deposition of H_2O_2 in Kyoto was estimated to be 11.7 mmol $m^{-2}\ y^{-1}$ in 1999 and 9.11 mmol $m^{-2}\ y^{-1}$ in 2000. H_2O_2 may be a dominant oxidant for SO_2 in the summer.

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 Japanese cedar and pine trees has been frequently reported in Japan.[3–5] Based on the acidity and chemical properties of soils, it is suggested that the acid-buffering capacity of the soils of mountains on three sides of the Kyoto basin will decrease considerably in the near future, as indicated by the 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 vary depending on the altitude.[7] Therefore, the role of air pollutants, such as atmospheric NO_2, SO_2, and O_3, which influence the biogeochemical cycles in mountains or forests, were investigated by passive samplers.[8–10] In Japan, the concentration level of atmospheric SO_2 became lower than that in 1970 by using natural gas or heavy oil containing low sulfur for power generation, although an equivalent reduction in the acidity and sulfate level in rainwater has not been observed.

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 at a pH less than 5.[11,12] 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.[11,13] H_2O_2 is also a toxic compound for plant cells, and might be another reagent responsible for forest decline.[14] However, few studies concerning the long-term behavior of H_2O_2 in the atmosphere and rainwater have been carried out in Japan.[15] Thus, in the present study, 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 role of atmospheric H_2O_2 on the origin of aqueous H_2O_2 in rainwater was investigated. Furthermore, the effect of H_2O_2 on the oxidation of SO_2 in rainwater was evaluated.

Experimental

Sampling Sites. Atmospheric H_2O_2 and aqueous H_2O_2 in rainwater were collected on the roof of the chemistry building (10 m height above the ground surface) at the Kyoto Institute of Technology (Sakyo-ku, Kyoto, Japan) since October, 1998. Aqueous H_2O_2 in rainwater was also collected at Iwakura, located about 4km northwest of the Kyoto Institute of Technology, since July, 1998.

Sampling Procedures for Ambient Air and Rainwater. Measurements of gas-phase hydrogen peroxide have been attempted by collecting the peroxide in aqueous solution using impingers or condensation collection devices.[16,17] However, these efforts have been shown to give unreliable results, due to the in situ formation of hydrogen peroxide from low-solubility constituents of ambient air and/or compressed air during collection.[18,19] It has been suggested that this artifact H_2O_2 may be formed by the decomposition of stable constituents, such as ozone,[20] or possibly by aqueous-phase recombination reactions of scavenged free radicals.[21] In the present work, a stripping coil was used according to a method of Yamashita et al.[15] The trapping system of atmospheric H_2O_2 is shown in Fig. 1. A stripping coil was constructed using Teflon tubing (2 mm i. d., length ca. 0.5 m). Air was sampled at a flow rate of 3 L/min through a glass-fiber prefilter (Millipore AP20). The stripping solution, which was 0.1 M potassium hydrogen phthalate in water adjusted to pH 6 with NaOH, was

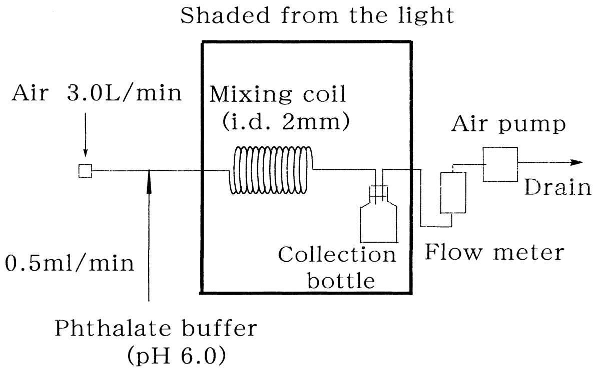

Fig. 1. Trapping system of atmospheric H_2O_2.

pumped into the inlet of the coil at a rate of 0.5 mL/min. A brown collection bottle was cooled with ice and shaded from the light. Atmospheric H_2O_2 was collected for 1 h and determined as soon as possible. The inlet of air was covered so as to avoid droplets.

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 two days. 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.

Measurement Procedure for H_2O_2 by Flow-Injection Analysis Based on the Peroxidase Enzyme Fluorescence Technique. The analytical procedure for peroxides is based on the peroxidase enzyme fluorescence technique developed by Lazrus et al.[22–24] This technique uses the formation of a fluorescent dimer from the reaction of peroxides, *p*-hydroxyphenylacetic acid (POPHA), and peroxidase for quantitation. This fluorescence technique for the determination of hydrogen peroxide also measures organic peroxides. In this study, the detected peroxides are considered to be primarily hydrogen peroxide because other work suggests that the major peroxide species in rain and cloud waters is hydrogen peroxide.[25–27]

The flow system for measuring H_2O_2 in the atmosphere and rainwater is schematically shown in Fig. 2. A sample containing H_2O_2 was injected by a sample injector (Rheodyne 7125) with a 300 μL loop. It was reacted with a mixing reagent of POPHA and horseradish peroxidase (HRP), and a fluorescent dimer was formed in a reaction coil. KOH was then added to the sample stream in order to maintain the fluorescence quantitum yield of the POPHA dimer. The fluorescence of the resulting dimer was monitored with a Shimadzu RF-10Axl fluorescence detector using an excitation wavelength of 320 nm and measuring the emission intensity at 400 nm. We used Iwaki peristaltic pumps and a Kimoto peristaltic pump. A Shimadzu chromatopac C-R5A was used for data analysis.

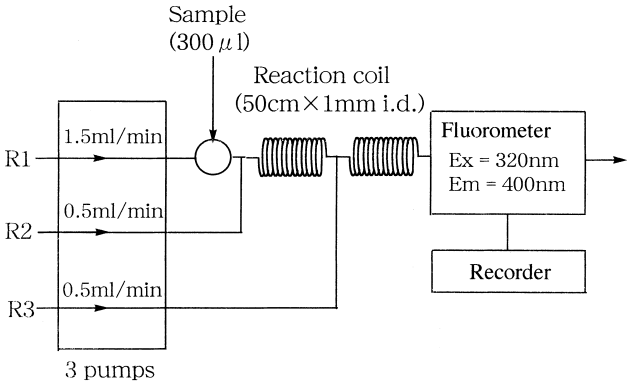

Fig. 2. Flow system for measuring H_2O_2.

Aqueous H_2O_2 standards were prepared by serial dilution of a stock H_2O_2 standard. The H_2O_2 concentration of the stock standard was determined by titration with $KMnO_4$. The stock H_2O_2 standard (1%) was prepared by diluting commercially available 30% H_2O_2, and then stored in a refrigerator. To prepare a 0.8 M POPHA solution, POPHA (Wako Pure Chemicals) was dissolved with 50 mL of ethanol. A solution of 2 mg/mL HRP was prepared by diluting HRP for biochemicals (Wako Pure Chemicals) in distilled water. These solutions were stored in a refrigerator and diluted with distilled water just before use. The reagent concentrations used by FIA were 1.6×10^{-4} M POPHA-0.04 mg/mL HRP and 0.05 M KOH for the determination of samples containing 0–0.5 μM H_2O_2 and 8×10^{-4} M POPHA-0.04 mg/mL HRP and 0.1 M KOH for the determination of samples containing 0.5–50 μM H_2O_2. All other chemicals were of the highest commercial grade. The relative standard deviations for this method are 0.5% (10 μM, $n = 5$) and 4.1% (0.1 μM, $n = 5$). The determination limit is 5×10^{-9} M (0.005 μM).

Results and Discussion

Diurnal and Seasonal Changes in the Atmospheric H_2O_2 Concentrations in Kyoto. The diurnal changes in the atmospheric H_2O_2 concentrations in Kyoto from April, 1999, to December, 1999, are shown in Fig. 3. The peak of atmospheric H_2O_2 occurred daily at 12:00–14:00, and was higher in the following order: December < April < June < September < August. The atmospheric H_2O_2 concentrations were larger in the daytime than at night, and the difference was small in the winter and large during the spring and summer. Even in the daytime, the H_2O_2 concentration became lower when the weather

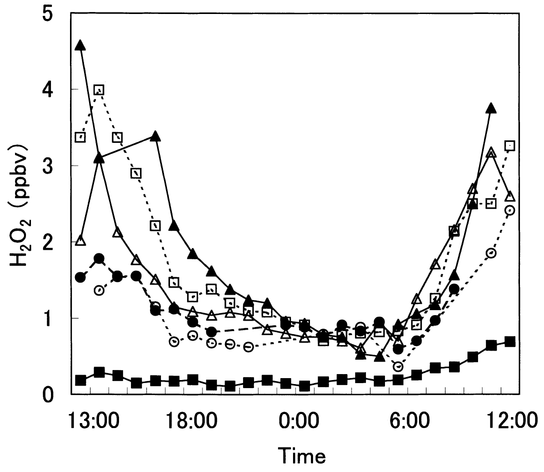

Fig. 3. Diurnal changes in atmospheric H_2O_2 concentrations in Kyoto: (○) April 8–9, (●) April 13–14, (△) June 3–4, (▲) August 20–21, (□) September 3–4, and (■) December 21–22, 1999.

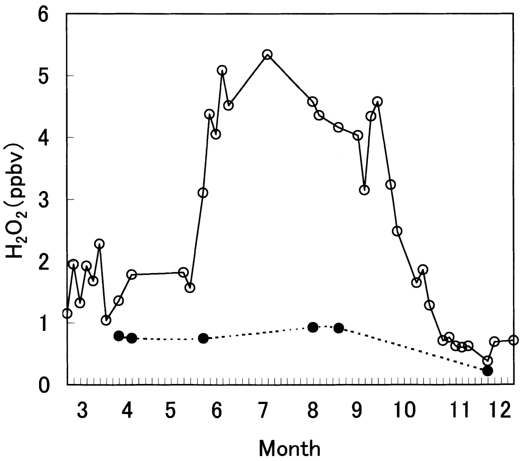

Fig. 4. Monthly changes in atmospheric H_2O_2 concentrations at 14:00 (daytime) and 2:00 (night) in Kyoto from March 1999 to December 1999: (○) 14:00 and (●) 2:00.

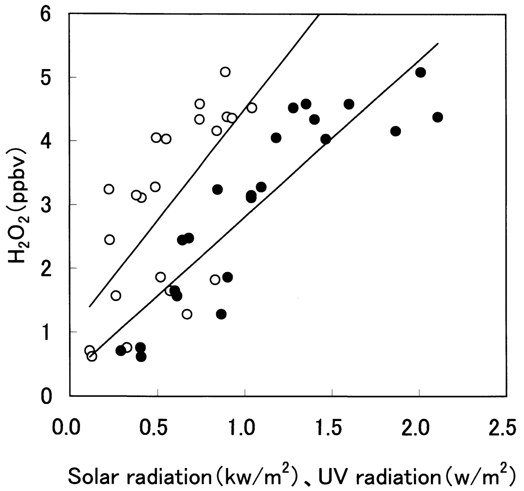

Fig. 5. Relationships between the concentrations of atmospheric H_2O_2 at 14:00 and solar radiation (○) or UV radiation (●).

changed from clear to cloudy skies. From these results, it could be concluded that the formation of atmospheric H_2O_2 may be due to a photochemical reaction. However, the minimum H_2O_2 concentrations at night from April to September were 0.5–0.95 ppbv, slightly larger than the daytime values during December. It is considered that a comparatively high H_2O_2 concentration at night from April to September may be attributed to the remaining H_2O_2, which was formed, but not decomposed in the daytime, or emissions from other sources of H_2O_2, such as stationary combustion facilities and automobiles.[15]

Monthly changes in the atmospheric H_2O_2 concentrations at 2:00 (night) and 14:00 (daytime) in Kyoto from March, 1999, to December, 1999, are shown in Fig. 4. The atmospheric H_2O_2 concentrations at 2:00 (night) were 0.75–0.93 ppbv from April to September and 0.19 ppbv in December. The atmospheric H_2O_2 concentrations at 14:00 (daytime) were 1–2 ppbv from March to May, and increased abruptly in June. Atmospheric H_2O_2 showed high values of 4–5.3 ppbv during June and September and decreased rapidly in late October, remaining at low levels of less than 1 ppbv from November to December. The atmospheric H_2O_2 concentrations in 2000, 0.09–5.8 ppbv, were similar to those in 1999. The average of the atmospheric H_2O_2 concentration in Kyoto from 1999 to 2000 was 1.3 ppbv. The seasonal variation of atmospheric H_2O_2 in Kyoto showed a summer maximum and a winter minimum. The higher H_2O_2 concentration in the summer may be due to the production of H_2O_2 by a photochemical reaction. The concentration range of atmospheric H_2O_2 was reported to be 0–3 ppbv in Hiroshima in June, September, and December, 1993,[15] and 0.2–2.9 ppbv in Okunikkou in August, 1998.[28]

Factors Affecting the Formation of Atmospheric H_2O_2. The factors affecting the formation of atmospheric H_2O_2, such as solar radiation, UV radiation, temperature, and relative humidity (RH) were investigated.

The relationships between the concentrations of atmospheric H_2O_2 at 14:00 and solar radiation (300–2800 nm) or UV radiation (280–315 nm) are shown in Fig. 5. The relationship between the concentrations of atmospheric H_2O_2 at 14:00 and solar radiation was positive (R^2 = 0.456). A better positive relationship was obtained between the concentrations of atmospheric H_2O_2 at 14:00 and UV radiation (R^2 = 0.790). High solar radiation and UV radiation levels may result in intense photochemical reactions of chemical species in the atmosphere, which can form free-radical species, including OH, RO, HO_2, and RO_2, from the photolysis of chemical species, such as formaldehyde and O_3.[29] Seasonal changes in the concentration of atmospheric H_2O_2 at 14:00, solar radiation, and UV radiation from March 1999 to December 1999 are shown in Fig. 6. The seasonal variation of atmospheric H_2O_2 in Kyoto showed a summer maximum and a winter minimum, while the levels of UV radiation and solar radiation were high from spring to summer and low in the winter. Although solar radiation and UV radiation in the spring were almost the same as those in the summer, the concentration of atmospheric H_2O_2

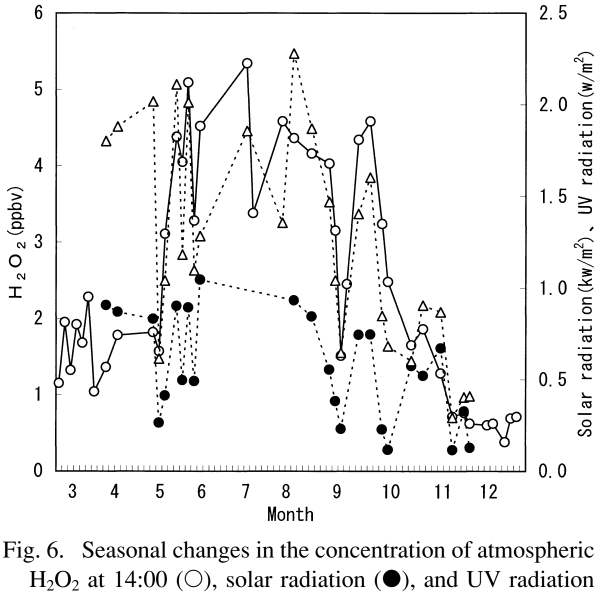

Fig. 6. Seasonal changes in the concentration of atmospheric H_2O_2 at 14:00 (○), solar radiation (●), and UV radiation (△) from March 1999 to December 1999.

in April was about 40% of those in August. The difference may result from the difference in the temperature: the mean temperatures in April and August were 12.7 °C and 26.4 °C, respectively.

Next, the effects of the air temperature and the relative humidity (RH) on the concentrations of atmospheric H_2O_2 were investigated. A quadratic relationship between the concentrations of atmospheric H_2O_2 and the air temperature were obtained by 24 h monitoring (Fig. 7). The concentrations of atmospheric H_2O_2 increased along with an increase in the air temperature, rising abruptly to above ca. 20 °C. A higher temperature may affect the reaction rate of the chemical species in the air, and enhance the production of OH and HO_2 free radicals, the precursors for H_2O_2. It has been reported that the OH radical increases along with an increase of the air temperature.[29] The concentration of atmospheric H_2O_2 was inversely correlated with RH, as shown in Fig. 8. In the daytime, the concentrations of atmospheric H_2O_2 decreased with an increase of RH, and the trend above 25 °C $\{y = -0.07x + 6.00$ $(R^2 = 0.543)\}$ was larger than that at 0–15 °C. The concentrations of atmospheric H_2O_2 decreased slightly with an increase of RH at night, being similar to that in the daytime at 0–15 °C.

On three successive days with different weather conditions (June 15–17, 1999), the concentrations of atmospheric H_2O_2 were examined (Fig. 9). The meteorological parameters, solar radiation, UV radiation, temperature and relative humidity are listed in Table 1. The atmospheric H_2O_2 concentration was highest on a clear day (June 16, 1999) and lowest on a rainy day (June 17, 1999). The results indicate that gaseous H_2O_2 may be easily removed from the atmosphere because Henry's law constant for H_2O_2 is relatively large (7.4×10^4 M atm^{-1} at 25 °C).[30]

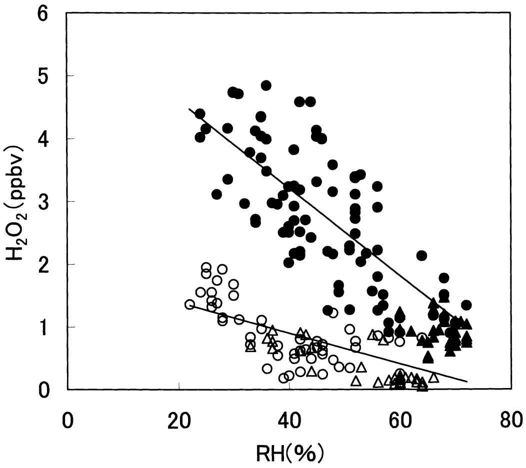

Fig. 8. Relationships between the concentration of atmospheric H_2O_2 and relative humidity (RH): (○) 0–15 °C (daytime), (●) ≧ 25 °C (daytime), (△) 0–15 °C (night), and (▲) ≧ 20 °C (night).

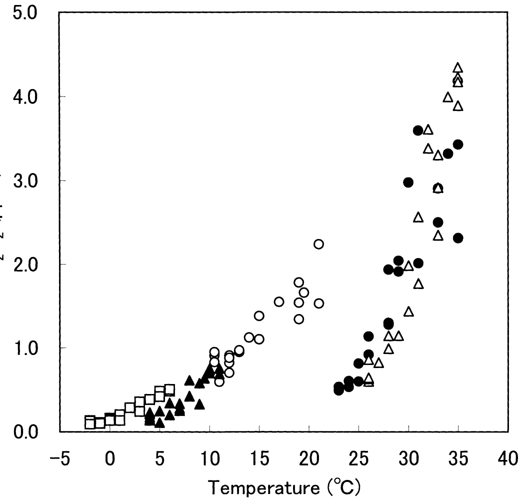

Fig. 7. Relationship between the concentrations of atmospheric H_2O_2 and air temperature: (○) April, (●) July, (△) August, (▲) November, and (□) December.

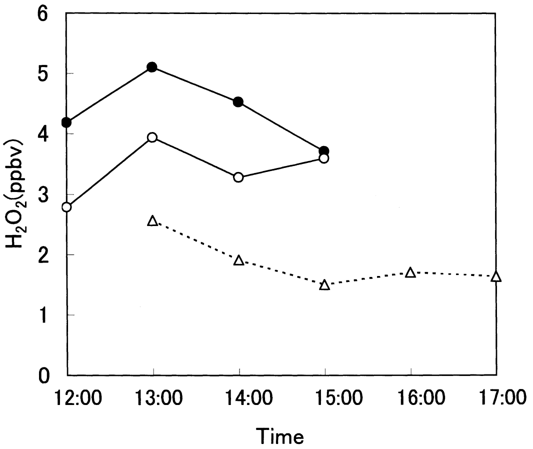

Fig. 9. Atmospheric H_2O_2 concentrations on three successive days with different weather conditions (June 15–17, 1999): (○) June 15, (●) June 16, and (△) June 17.

Table 1. Meteorogical Parameters on Three Successive Days with Different Weather Conditions (June 15–17, 1999)

Weather	Temp	RH	UV radiation	Solar radiation
	°C	%	W m^{-2}	kw m^2
Cloudy day (6/15)	34	41	1.51	0.59
Clear day (6/16)	37	29	1.65	0.63
Rainy day (6/17)	30	49	0.49	0.17

*The values at 14:00 are listed.

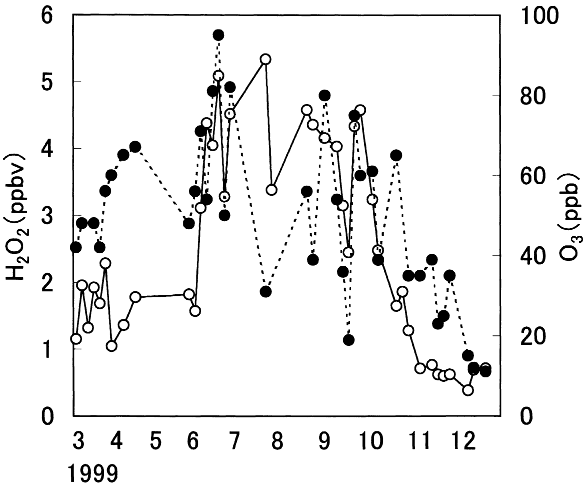

Fig. 10. Monthly changes in atmospheric concentrations of H_2O_2 and O_3 at 14:00 in Kyoto: (○) H_2O_2 and (●) O_3.

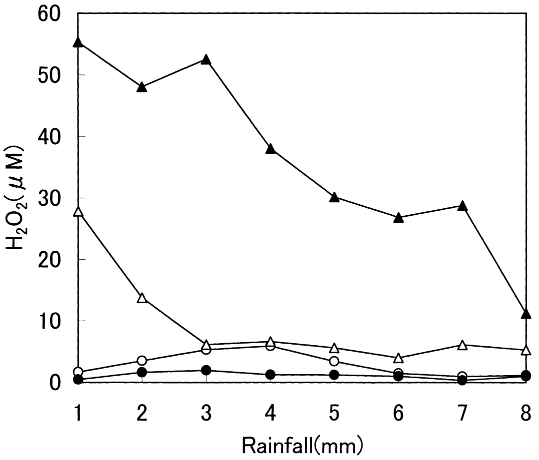

Fig. 11. Time variations of H_2O_2 concentrations per 1 mm of precipitation in Kyoto: (○) January 19, (●) February 11, (△) June 26, and (▲) July 18.

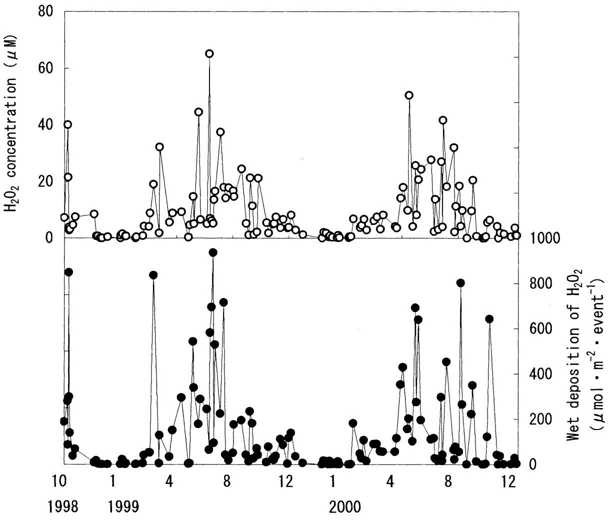

Fig. 12. Seasonal changes in H_2O_2 concentration in rainwater and wet deposition of H_2O_2 during one event.

Atmospheric H_2O_2 and O_3. The behavior of atmospheric O_3 in the mountains around the Kyoto basin has been measured since May, 1997.[9,10] The behavior of atmospheric O_3 was then compared with that of atmospheric H_2O_2 from March, 1999, to December, 1999. The relationships between the concentrations of atmospheric H_2O_2 and O_3 were $y = 0.035x + 0.357$ ($R^2 = 0.347$) in the daytime (sample number, $n = 184$). These values were not correlated well at night ($R^2 = 0.068$, $n = 65$). The peak of the atmospheric H_2O_2 occurred at 12:00–14:00, and decreased rapidly after sunset, while the concentration of atmospheric O_3 was also high at 12:00–15:00 and decreased rapidly during the night due to O_3 scavenging by NOx; however, that in April did not decrease very much. Fig. 10 shows the monthly changes in the atmospheric concentrations of H_2O_2 and O_3 at 14:00 from March, 1999, to December, 1999. The seasonal variation of atmospheric H_2O_2 at 14:00 showed a clear pattern with a maximum during the summer months (June–September) and a winter minimum, while that of O_3 exhibited the highest values in the spring, summer, and fall. The concentration of O_3 in the winter was only about half the summer level, but still relatively high compared with that of atmospheric H_2O_2 in the winter. The higher concentration of O_3 in the spring could be explained by the combination of less destruction at night and larger injection from the stratosphere than in other seasons.[31–33] Atmospheric O_3 may have its origin in both stratospheric input and O_3 production by a photochemical reaction.[9,10] On the other hand, atmospheric H_2O_2 may be mainly produced by a photochemical reaction.

Behavior of H_2O_2 in Rainwater. The time variations of the H_2O_2 concentration per 1 mm of precipitation are shown in Fig. 11. The H_2O_2 concentration in rainwater was highest at the beginning of rainfall, and became lower in the summer. On the other hand, the H_2O_2 concentration in rainwater was very low even at the beginning of rainfall, its change with time being small in the winter. Seasonal changes in the H_2O_2 concentration in rainwater and wet deposition of H_2O_2 during one event are shown in Fig. 12. The H_2O_2 concentration in rainwater showed a high level with 1.2–65.1 μM from June to August, while maintaining a low level of less than 0.01 μM in the winter. The wet deposition of H_2O_2 in the summer was much greater than that in the winter. The seasonal variations of aqueous H_2O_2 in rainwater and the wet deposition of H_2O_2 showed a summer maximum and a winter minimum, which were similar to the trend of atmospheric H_2O_2. Furthermore, the H_2O_2 concentration in rainwater decreased as the amount of rainfall increased. Next, the H_2O_2 concentrations in rainwater during the daytime (6:00–18:00) were compared with those during the night (18:00–6:00) (Table 2). The H_2O_2 concentrations in rainwater during the daytime were higher than those during the night, which was also similar to the trend of atmospheric H_2O_2. These results indicate that gaseous H_2O_2 may be rapidly removed from the atmosphere by wet deposition and aqueous H_2O_2 in rain may originate mostly from gas-phase H_2O_2.

The volume-weighted averages of the H_2O_2 concentration in 1999 and 2000 were 7.47 μM and 6.70 μM, respectively. The rain amounts in 1999 and 2000 were 1.57 m y^{-1} and 1.36 m y^{-1},

Table 2. Comparison of H_2O_2 Concentrations in Rainwater during the Daytime with Those during Night

	H_2O_2 concentration (μmol L^{-1})					
	Summer		Winter		All	
	daytime	night	daytime	night	daytime	night
Average	23.59	12.93	1.66	1.64	12.92	5.92
	(n = 13)	(n = 6)	(n = 12)	(n = 11)	(n = 29)	(n = 21)
Max.	65.05	21.20	6.64	8.46	65.06	21.20
Min.	2.18	1.16	0.11	0.00	0.11	0.00

respectively. Then, the wet deposition of H_2O_2 in Kyoto was calculated to be 11.7 mmol m^{-2} y^{-1} in 1999 and 9.11 mmol m^{-2} y^{-1} in 2000. Although other data of H_2O_2 wet deposition in Japan have not been reported, wet deposition of H_2O_2 in the U.S.A. was reported to be 1.5 mmol m^{-2} y^{-1} (0.34 m y^{-1} rainfall) in the Los Angeles Basin, California during 1985–1991[26] and 12 mmol m^{-2} y^{-1} (9.6 μM H_2O_2 concentration, 1.3 m y^{-1} rainfall) in Wilmington, North Carolina during 1992–1994.[34] The wet deposition of H_2O_2 in Kyoto is relatively similar to that in Wilmington, North Carolina, and much greater than that in the Los Angeles Basin, California. Wet deposition of H_2O_2 in Kyoto was estimated to be 38% of the total deposition by using an average gas-phase concentration of 1.3 ppbv and a deposition velocity of 1.0 cm s^{-1} for gas-phase H_2O_2.[35] From these results, it is considered that the wet deposition of H_2O_2 depends on the presence of pollutants which consume H_2O_2, rainfall and humidity in the region. Moreover, the wet deposition of H_2O_2 in the summer (June–September) was estimated to be more than 60% of the annual wet deposition, while that in the winter (November–February) was less than 10%. These results suggest that the wet deposition of H_2O_2 in the summer is much greater than that in the winter.

Chemical Components and pH in Rainwater. The concentrations of chemical components and pH in rainwater has been measured since 1994 in Kyoto. The pH values ranged from 3.30 to 6.60 with a mean of 4.50. The pH values of rain samples in the summer were lower than those in other seasons. The relationship between the equivalent concentration of $\{[\text{non sea-salt (nss)-}SO_4^{2-}] + [NO_3^-]\} - \{[NH_4^+] + [\text{nss-}Ca^{2+}]\}$ and the pH is shown in Fig. 13. When the equivalent concentration of $\{[\text{nss-}SO_4^{2-}] + [NO_3^-]\} - \{[NH_4^+] + [\text{nss-}Ca^{2+}]\}$ was high, the pH of a sample was low. The annual mean equivalent ratios of NO_3^-/nss-SO_4^{2-} in Kyoto, 0.62–0.82, from 1994 to 2000 were larger than the mean value in Japan, 0.34, and similar to those of large cities such as Tokyo and Osaka.[36] The annual mean equivalent ratios of NO_3^-/nss-SO_4^{2-} at pH less than 4.0, 4.0–5.0, and more than 5.0 were 1.04, 0.84 and 0.48, respectively. The values increased with a decrease in the pH. Both nitric and sulfuric acids contributed to the precipitation acidity in Kyoto, but the contribution of nitric acid was larger than that of sulfuric acid at low pH. These results indicate that Kyoto has low pH precipitation during the summer due to the high contribution of acidic sources with sulfuric acid and nitric acid emitted domestically, which is similar to areas close to the Pacific Ocean.[37]

Effect of H_2O_2 on the Oxidation of SO_2 in Rainwater. The volume-weighted averages of the SO_4^{2-} concentration in 1999 and 2000 were 10.8 μM and 13.0 μM, respectively. The wet deposition of SO_4^{2-} in Kyoto was 17.0 mmol m^{-2} y^{-1} in 1999, and was 17.7 mmol m^{-2} y^{-1} in 2000. The seasonal change in the SO_4^{2-} concentration in rainwater did not show a regular pattern, which is similar to the pattern of atmospheric SO_2. The concentration range of atmospheric SO_2 at a public station (Sakyo-ku, Kyoto) was 2.6–6.1 ppb during 1996–1999,

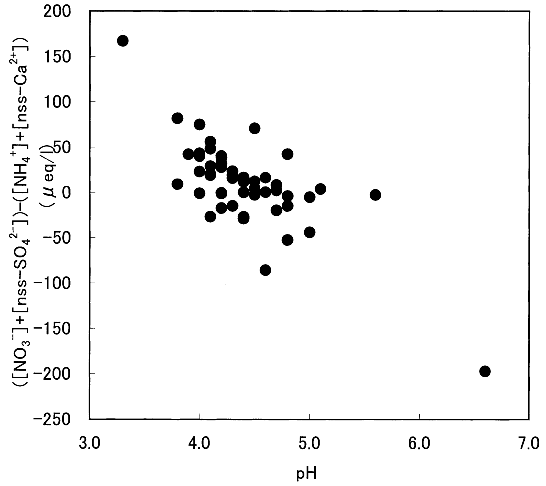

Fig. 13. Relationship between the equivalent concentration of $\{[\text{nss-}SO_4^{2-}] + [NO_3^-]\} - \{[NH_4^+] + [\text{nss-}Ca^{2+}]\}$ and pH.

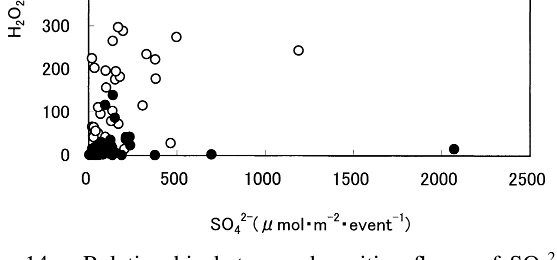

Fig. 14. Relationship between deposition fluxes of SO_4^{2-} and H_2O_2 in summer (○) and winter (●).

which remaining fairly constant throughout the year. In order to evaluate the effect of H_2O_2 on the oxidation of SO_2 in rainwater, the relationships between the SO_4^{2-} and H_2O_2 deposition fluxes of one event in the summer (June–September) and winter (November–February) are shown in Fig. 14. Although a positive relation was obtained in the summer ($R^2 = 0.667$), no relation was obtained in the winter ($R^2 = 0.010$). That no relation occurred in the winter may have resulted from the lower concentration of H_2O_2 compared with SO_2. These results suggest that H_2O_2 may greatly determine the formation of sulfuric ion in rainwater during the warm season, while O_3, and O_2 catalyzed by Fe and Mn may be dominant oxidants for SO_2 in the winter.

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