Measurements of Atmospheric Peroxides Concentrations

Near the Summit of Mt. Norikura in Japan

By Koichi Watanabe, Yutaka Ishizaka and Hiroshi Tanaka

*Institute for Hydrospheric-Atmospheric Sciences, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan**(Manuscript received 10 August 1995, in revised form 25 October 1995)*

Abstract

Concentrations of gaseous peroxides and other trace gases (O_3 , SO_2) have been measured near the summit of Mt. Norikura (altitude, 2770 m) in central Japan, during summer and early autumn. Hydrogen peroxide (H_2O_2) and O_3 reached the maximum concentrations at midnight and the minimum at midday. The maximum concentrations of H_2O_2 and O_3 appearing at midnight are likely to be caused by subsidence from a higher atmospheric level. This tendency is quite opposite to that appearing in the low-altitude flat areas. The ratio of $[H_2O_2]/[SO_2]$, which is a useful indicator of the oxidizing capacity from $SO_2(S(IV))$ to $H_2SO_4(S(VI))$, was almost larger than 1 during summer. This means that oxidant of SO_2 is plentiful in the summer season and is likely to accelerate the heterogeneous oxidation in atmospheric water droplets.

1. Introduction

Peroxides are important trace gases which play significant roles on the chemical cycle in the atmosphere. Hydrogen peroxide (H_2O_2) is the major peroxide, mainly formed by the reaction of two hydroperoxy radicals (HO_2):

The HO_2 is generated from both ozone (O_3) photolysis and photochemical degradation of hydrocarbons (Calvert and Stockwell, 1983). Therefore, H_2O_2 concentration is affected by the atmospheric pollutants and the meteorological conditions (Sakugawa *et al.*, 1990). In addition, H_2O_2 is the most important oxidizing agent for the conversion of SO_2 to H_2SO_4 in atmospheric liquid water, thereby contributing to the acidification of cloud and rain waters. The oxidation of dissolved $SO_2(S(IV))$ by H_2O_2 is particularly important, because it rapidly proceeds when pH values are lower than 5. In contrast, the reaction rate of $S(IV)$ by O_3 rapidly decreases with decreasing pH (Martin and Damschen, 1981).

In addition to H_2O_2 , organic hydroperoxides (ROOH) are present in the atmosphere and are likely to be effective in the oxidation of aqueous SO_2 (Lind *et al.*, 1987). Organic hydroperoxides are formed by reactions of the hydroperoxy radical (HO_2) and the organic peroxy radical (RO_2):

where R represents an alkyl or acyl group. Large abundance of ROOH is now thought to be produced by reactions of naturally originating hydrocarbons (terpenes and isoprenes) with O_3 via a Criegee bi-radical intermediate (Gäb *et al.*, 1985; Hewitt and Kok, 1991; Simonaitis *et al.*, 1991). Actually, ROOH concentrations in forest areas seen to be higher. The reactions are written as:

The Criegee bi-radical (RCHOO) obtained by the reaction (3) reacts with H_2O to form a ROOH. In the case where R is CH_2 , hydroxymethylhydroperoxide (HMHP, $HOCH_2OOH$) is produced:

Forests are exposed to ambient chemical and physical stresses which are harmful to some species of trees, especially in Europe and the United States (Prinz, 1987; Aneja and Li, 1992). Peroxides are possible candidates which damage vegetation, as well as O_3 (Masuch *et al.*, 1986; Ennis *et al.*, 1990).

Measurements of the atmospheric peroxides and other trace gases (O_3 , SO_2 , NO_x) at high-elevation sites near the summit of a mountain are important, not only to estimate the concentrations in the free troposphere but also to investigate the acidification processes of mountain fog water. Observations at a mountain top have been performed at some stations in the United States and Europe (Olszyna *et*

Fig. 1. Map of central Japan showing location of Mt. Norikura and Wajima.

et al., 1988; Meagher *et al.*, 1990; Claiborn and Aneja, 1991; Gallagher *et al.*, 1991; Aneja *et al.*, 1994). The concentrations of H_2O_2 and O_3 were larger at the mountain sites than at ground level (Claiborn and Aneja, 1991; Sakugawa and Kaplan, 1993). It has been reported that the potential capacity of SO_2 oxidation depends on the season because H_2O_2 concentration shows a clear seasonal variation (Meagher *et al.*, 1990). However, H_2O_2 concentration has not so far been investigated in high mountain areas in Japan, which is frequently covered with strongly acid fog.

In this paper, we report the characteristics of concentrations of atmospheric peroxides (H_2O_2 and ROOH (semi-quantitative)) and other trace gases (O_3 , SO_2) measured near the top of Mt. Norikura, located in central Japan, during several months in the summer and early autumn seasons in 1993 and 1994. Our results show the likelihood of assumed functions and processes of peroxides in the atmosphere.

2. Method

Measurements of atmospheric peroxides and other trace gases (O_3 and SO_2) were made at the Norikura Observatory of the Institute for Cosmic Ray Research (altitude 2770 m), University of Tokyo, located near the summit of Mt. Norikura in central Japan (Fig. 1). The observations were performed in July and September in 1993 and from July to

Fig. 2. Schematic of the sampling equipment.

September in 1994. Unfortunately, the SO_2 concentration could not be measured in both Septembers.

Gaseous H_2O_2 was collected by the cold-trap method (Sakugawa and Kaplan, 1987). The gas sampler was a glass cold trap (-70°C to -60°C) shown in Fig. 2 with a 3.0 cm I.D. $\times$ 40 cm (outside tube) and a 1.5 cm I.D. $\times$ 35 cm (inside tube). Ambient air passed through a cooled gas trap in which H_2O_2 was trapped together with water vapor. This method was not affected by interference of O_3 (Sakugawa and Kaplan, 1987). The air was sucked at a flow rate of 2.5 ℓ/min and the sampling time was 2 hours. The collection efficiency was 100 %. After the collection, the frozen water vapor was defrosted. Hydrogen peroxide concentration was determined by the fluorometric method used by Lazrus *et al.* (1985). The fluorescence reagents, 1 ml *p*-hydroxyphenyl acetic acid (1.5×10^{-2} M) in 0.03 M phosphate buffer (adjusted to pH 7) and 1 ml peroxidase (50 unit ml^{-1}) in 0.03 M phosphate buffer, were added to the defrosted liquid sample immediately after the sampling. Several minutes later, 1 ml NaOH (1N) was added to stabilize the generated fluorescence. The amount of fluorescence in the solution was determined by a fluorometer (Shimadzu Corporation, Model RF-5000), of which the excitation and emission wavelengths are 320 and 400 nm, respectively. This method determines the concentration of total peroxides (H_2O_2 and organic hydroperoxides). To discriminate H_2O_2 from organic hydroperoxides (ROOH), catalase reagent was added to the sample before adding the fluorescence reagents because H_2O_2 is more rapidly decomposed by catalase. The concentration of catalase was adjusted to decompose about 70 % of H_2O_2 . Hydrogen peroxide concentration in the liquid phase was calculated from the decomposition efficiency of the catalase reagent and the difference between the values obtained with and without the catalase reagent. According to Hellpointner and Gb (1989) the calibration curves for freshly prepared equimolar of H_2O_2 and methylhydroperoxide (MHP, CH_3OOH), which is the predominant compound of

Fig. 3. Time variations of peroxides concentrations (upper panel) and dewpoint temperature (lower panel) near the summit of Mt. Norikura during 14–17 September in 1993.

ROOH, were identical. However, we did not examine the collection efficiency of ROOH by the cold-trap (-70°C to -60°C) method. Fels and Junkermann (1994) sampled peroxides at liquid nitrogen temperature and determined the individual ROOH components by high-performance liquid chromatography (HPLC). Cold-trap (cryogenic) sampling at liquid nitrogen temperature may be superior in the collection efficiency of ROOH to that at -70°C . Therefore, we treat the measured ROOH concentrations as semi-quantitative values. Concentrations of gaseous H_2O_2 and ROOH (semi-quantitative) were calculated from H_2O_2 and ROOH concentrations of trapped solution and water vapor content.

Ozone was measured by means of an ultra violet absorption technique (Thermo Electron Corporation O_3 Analyser, Model 49). The detection limit of the analyzer is about 5 ppbv. Sulfur dioxide was measured by the pulse fluorometric method (Thermo Electron Corporation SO_2 Analyser, Model 43S). The detection limit of the SO_2 analyzer is about 0.1 ppbv.

For meteorological data analysis, we used Aerological Data of Japan for Wajima Weather Station located 150 km north of Mt. Norikura (Fig. 1) during August in 1994 (Japan Meteorological Agency, Tokyo, 1994).

Fig. 4. Time variations of peroxides (H_2O_2 and ROOH (semi-quantitative)), O_3 and SO_2 concentrations near the summit of Mt. Norikura during 6–9 July in 1994.

3. Results

Figure 3 shows the gaseous total peroxides concentrations and dewpoint temperature measured during September in 1993. Here, we do not divide the total peroxides into hydrogen peroxide (H_2O_2) and organic hydroperoxides (ROOH). During 13–14 September the sampling site was covered with dense fog in precipitating condition associated with a stagnant frontal system, and, therefore, the concentrations of gaseous peroxides were very low. During 15–17 September a high-pressure system covered central Japan and the sky of the sampling site cleared up, except that thin fog often passed through the site during the nighttime of 15–16 September. Maximum concentration of the total peroxides was observed at midnight, and minimum concentration appeared in the daytime. This diurnal variation is opposite to that observed at the ground level, where daytime concentration is larger than nighttime concentration.

This opposite pattern of diurnal variation observed at a high elevation site is caused by the air circulation associated with a mountainous region. Air parcels at lower altitude, in which peroxides concentrations is low, is transported by upslope wind during the daytime. On the other hand, at night, the sampling site is exposed to peroxides-rich air transported from the free atmosphere. The variation of dewpoint temperature provides the evidence of such vertical air motions. High dewpoint temperature air brought by the lower atmosphere was observed in the daytime, and low dewpoint temperature air transported from the higher atmosphere appeared at night.

The results of the measurements of the trace gases, peroxides, O_3 and SO_2 , during several days of summer season in 1994 are demonstrated in Figs. 4, 5 and 6. Through the periods shown at the fig-

Table 1. Summary of gaseous H_2O_2 concentrations near the summit of Mt. Norikura (altitude, 2770 m) during the summer and early autumn in 1994. Gaseous concentrations are parts per billion by volume and values are 2-hour sampling data. N and SD denote the number of samples and standard deviation, respectively.

Period	N	Mean	SD	Minimum	Maximum
July	38	1.5	0.95	0.15	4.5
August	31	1.1	0.75	0.10	3.1
September	17	0.7	0.41	0.10	1.5

Fig. 5. Time variations of peroxides (H_2O_2 and ROOH (semi-quantitative)) and O_3 concentrations near the summit of Mt. Norikura from 30 July to 2 August in 1994.

ures, the sampling site was cleared except that it was sometimes covered with fog during 6–7 July. Hydrogen peroxide concentrations ranged from 0.1 to 4.5 ppbv during the periods of measurements, and the concentrations were about the same as those measured at the mountain sites in the United States (Claiborn and Aneja, 1991; Sakugawa and Kaplan, 1993; Aneja *et al.*, 1994). The large H_2O_2 concentrations were observed at night. On the other hand, organic hydroperoxides (ROOH) concentrations increased in the daytime and sometimes exceeded the H_2O_2 concentrations.

Ozone concentrations varied from 10 to 72 ppbv and were larger at night than in the daytime. Concentrations of SO_2 were less than 0.6 ppbv and larger in the daytime than at night. Sulfur dioxide concentrations observed near the top of Mt. Norikura were much lower than that observed near the top of mountains in the United States. A summarized list of the gaseous H_2O_2 concentrations measured in 1994 is given on Table 1. The data show the sea-

Fig. 6. Time variations of peroxides (H_2O_2 and ROOH (semi-quantitative)) and O_3 concentrations (upper panel) and dew-point temperature (lower panel) near the summit of Mt. Norikura during 27–28 August in 1994.

sonal variation and that the mean concentration in July is significantly larger than that in September.

4. Discussion

Near the summit of Mt. Norikura (altitude 2770 m), mean diurnal variation patterns of the concentrations of peroxides (H_2O_2 and ROOH), O_3 and SO_2 on clear days during the summer in 1994 are shown in Fig. 7. The highest concentration of H_2O_2 was observed at midnight and the lowest concentrations appeared at midday. This variation pattern of H_2O_2 concentration is different from the current understanding of H_2O_2 photochemistry. The nighttime maximum of H_2O_2 concentration near the summit of Mt. Norikura is opposite to that reported in the low altitude areas. For example, in the city of Nagoya, a maximum H_2O_2 concentration was observed in the afternoon, corresponding to a minimum of NO_x concentration and a few hours after a maximum of O_3 concentration (Watanabe and Tanaka, 1995). A similar variation was observed in Los Angeles (Sakugawa and Kaplan, 1989). Recently, nocturnal maxima in H_2O_2 concentration have been observed at some mountain-top sites (Claiborn and Aneja, 1991; Ross *et al.*,

Fig. 7. Mean diurnal variations of peroxides (H_2O_2 and ROOH (semi-quantitative)), O_3 and SO_2 concentrations in July and August in 1994.

1992; Aneja *et al.*, 1994). Ozone concentration near the summit of Mt. Norikura was also larger at night than in the daytime, though the variation amplitude is smaller than that of H_2O_2 . The nocturnal peaks in both H_2O_2 and O_3 concentrations are more likely to be caused by the atmospheric transports rather than chemical reactions.

Hydrogen peroxide concentration usually increases with height (Kleinman and Daum, 1991). Concentration of nighttime H_2O_2 is maintained as large as that of daytime above the planetary boundary layer (Kleinman, 1986; Van Valin *et al.*, 1987). The elevation of the present observation site is higher than the top of the planetary boundary layer at night. In the daytime, however, the lower atmosphere is transported to the sampling site by the upslope wind, and the sampling location is shrouded in the mixing layer in which the H_2O_2 concentration may be lower. Moreover, in this process, the upslope wind passes through a forest which acts to reduce the concentrations of H_2O_2 and O_3 in the atmosphere. The deposition of H_2O_2 to vegetation surfaces is very large (larger than that of O_3) (Ennis *et al.*, 1990). Therefore, the diurnal variation amplitude of H_2O_2 concentration is larger than that of O_3 concentration at the mountain-top site. The larger concentration of H_2O_2 at the sampling site is very likely to have subsided from a higher region in which the nighttime H_2O_2 concentration is as large as the daytime H_2O_2 concentration.

The diurnal variation can also be elucidated by the meteorological data analysis. As an example, we will discuss the result obtained on 27–28 August in 1994 (Fig. 6). During this period, Japan was widely covered with the Pacific high pressure system. The vertical profiles of dewpoint temperature during this time at Wajima Weather Station are shown in Fig. 8. The dewpoint temperatures decreased with altitude. The pressure at the summit of Mt. Norikura

Fig. 8. Vertical profiles of dewpoint temperature at Wajima Weather Station. (A) at 20:30 on 27 August in 1994 (B) at 8:30 on 28 August in 1994

was about 730 hPa. The dewpoint temperature at 730 hPa was about 5°C in the evening on 27 August and fell down to about 0°C in the morning on 28 August. At the sampling location, the dewpoint temperature was 4.1°C at 22 h on 27 August and gradually fell to 0°C at midnight. The decline in dewpoint temperature is due to air subsidence. At the same time, the concentrations of H_2O_2 and O_3 reached a maximum value (Fig. 6). The dewpoint temperature remained at about 0°C until early the next morning. Such a variation of dewpoint temperature at Mt. Norikura is consistent with the vertical profiles shown in Fig. 8.

The dewpoint temperature rose up to 8.5°C at 8 h and then reached 10°C at noon on 28 August. Hydrogen peroxide and O_3 concentrations reached a minimum value at noon. According to the vertical profile (B) shown in Fig. 8, the pressure altitude at which the dewpoint temperature is 10°C is lower than 800 hPa. Therefore, the air parcel at the foot of the mountain would be transported up to the sampling site.

Organic hydroperoxides (ROOH) concentrations in the daytime were significantly larger than those at night, though the concentrations were semi-quantitative. The predominant compounds of ROOH are methylhydroperoxide (MHP, CH_3OOH) and hydroxymethylhydroperoxide (HMHP, HOCH_2OOH) (Fels and Junkermann, 1994). These organic hydroperoxides are produced by the chemical reaction of O_3 with natural hydrocarbons released from the forest (Gäb *et al.*, 1985; Becker *et al.*, 1990; Hewitt and Kok, 1991; Simonaitis *et al.*, 1991), except that those are produced in polluted air. Organic hydroperoxides compounds are now thought to play an important role in the oxidation

Fig. 9. Frequency distributions of the $[H_2O_2]/[SO_2]$ ratio near the summit of Mt. Norikura during the summer season in 1993 and 1994.

of S(IV) toward S(VI) in the aqueous phase, as well as H_2O_2 (Lind *et al.*, 1987; Hewitt *et al.*, 1990). The elevation of the sampling site is much higher than the tree line. Therefore, there is one possibility that ROOH produced in the lower forest area may be transported by the upslope wind in the daytime. However, we need to make more detailed observations to elucidate the phenomenon exactly.

Hydrogen peroxide is the most important oxidant for SO_2 oxidation. The ratio of $[H_2O_2]/[SO_2]$ is a useful indicator of the potential capacity to oxidize S(IV) to S(VI). The condition $[H_2O_2] < [SO_2]$ is called *oxidant limitation* in which there is a non-linear relationship between SO_2 concentration in the air and H_2SO_4 produced in the aqueous phase (Calvert *et al.*, 1985; Kleinman, 1986; Meagher *et al.*, 1990). Frequency distributions of $[H_2O_2]/[SO_2]$ near the summit of Mt. Norikura during the summer season in 1993 and 1994 are shown in Fig. 9. Most of the cases show the condition $[H_2O_2] > [SO_2]$, which implies the existence of sufficient oxidant of SO_2 . Even for the condition $[H_2O_2] < [SO_2]$, total peroxides ($[H_2O_2] + [ROOH]$) concentrations exceeded the SO_2 concentration. This case is different from those of Whiteface Mountain, Whitetop Mountain and Mt. Mitchell in the eastern United States, where oxidant limitation cases were frequently found, even in the summer season (Meagher *et al.*, 1990; Claiborn and Aneja, 1991). These mountainous areas have been frequently covered with strongly acidic fogs. Sulfate ion (SO_4^{2-}) concentrations in the fog water showed seasonal variations; that is, SO_4^{2-} concentrations in the summer season when oxidation capacity is higher were larger than those in other

seasons (Mohnen and Kadlec, 1989; Saxena *et al.*, 1989).

At Mt. Norikura, strongly acidic fogs ($pH < 4$) have been also frequently observed during the summer season and sulfate ions have been detected as the most predominant anion in the fog water (Okita, 1968; Qian *et al.*, 1992; Minami and Ishizaka, 1995). The concentration of H_2O_2 in fog water was very large during summer (in our unpublished report). Therefore, if SO_2 concentration in the air rises during summer, even if slightly, acidic fog may easily be produced in the sufficient-oxidant circumstances. Acidification of fog water is suppressed in the condition that H_2O_2 concentration is at low levels, as in winter.

5. Conclusions

Measurements of gaseous peroxides (H_2O_2 , ROOH), O_3 and SO_2 concentrations have been conducted near the summit of Mt. Norikura (altitude, 2770 m), located in central Japan, during the summer (and the early autumn) in 1993 and 1994. Hydrogen peroxide and O_3 concentrations on Mt. Norikura ranged from 0.1 to 4.5 ppbv and 10 to 72 ppbv, respectively. The mean concentration of H_2O_2 in summer was significantly larger than that in autumn.

Hydrogen peroxide concentration showed clear diurnal variations. The maximum concentration appeared at midnight, and the minimum concentration was observed at midday. Ozone concentration was also larger at night than in the daytime. This nocturnal predominance of H_2O_2 and O_3 concentrations at the high elevation site is caused by meteorological processes rather than chemical processes. In the daytime, the lower air is transported by an upslope wind, but the higher air (H_2O_2 -rich) subsides at night. Such processes were supported by the meteorological data analysis. On the other hand, organic hydroperoxides (ROOH) concentrations increased in the daytime.

The ratio of $[H_2O_2]/[SO_2]$ was mostly larger than 1 in the summer season. Such a condition shows a sufficient oxidation potential for SO_2 oxidation. Therefore, even if SO_2 concentration increases slightly during the summer in this region, acidification of fog water may easily be accelerated.

Acknowledgments

We would like to thank Profs. H. Terai and K. Kato and Drs. H. Tsuruta and C. Takenaka and Y. Minami, K. Matsumoto, T. Kuwahara and S. Hamajima for their support on the observations. We also present special thanks to the members of the Norikura Observatory of the Institute for Cosmic Ray Research, University of Tokyo. This study was supported in part by the Grant-in-Aid for Scientific Research, the Ministry of Education, Science

and Culture of Japan and a fund of Nippon Life Insurance Foundation.

References

- Aneja, V.P. and Z. Li, 1992: Characterization of ozone at high elevation in the Eastern United States: trends, seasonal variations and exposure. *J. Geophys. Res.*, **97**, 9873–9888.
- Aneja, V.P., C.S. Claiborn, Z. Li and A. Murthy, 1994: Trends, seasonal variations, and analysis of high-elevation surface nitric acid, ozone and hydrogen peroxide. *Atmos. Environ.*, **28**, 1781–1790.
- Becker, K.H., K.J. Brockmann and J. Bechara, 1990: Production of hydrogen peroxide in forest air by reaction of ozone with terpenes. *Nature*, **346**, 256–258.
- Calvert, J.G. and W.R. Stockwell, 1983: Acid generation in the troposphere by gas-phase chemistry. *Envir. Sci. Technol.*, **17**, 428A–443A.
- Calvert, J.G., A.L. Lazrus, G.L. Kok, B.G. Heikes, J.G. Welega, J. Lind and C.A. Cantrell, 1985: Chemical mechanisms of acid generation in the troposphere. *Nature*, **317**, 27–35.
- Claiborn, C.S. and V.P. Aneja, 1991: Measurements of atmospheric hydrogen peroxide in the gas phase and in cloud water at Mt. Mitchell, North Carolina. *J. Geophys. Res.*, **96**, 18771–18787.
- Ennis, C.A., A.L. Lazrus, P.R. Zimmerman and R.K. Monson, 1990: Flux determination and physiological response in the exposure of red spruce to gaseous hydrogen peroxide, ozone and sulfur dioxide. *Tellus*, **42**, 183–199.
- Fels, M. and W. Junkermann, 1994: The occurrence of organic peroxides in air at a mountain site. *Geophys. Res. Lett.*, **21**, 341–344.
- Gäb, S., E. Hellpointner, W.V. Turner and F. Korte, 1985: Hydroxymethyl hydroperoxide and bis (hydroxymethyl) peroxide from gas-phase ozonolysis of naturally occurring alkenes. *Nature*, **316**, 535–536.
- Gallagher, M.W., T.W. Choularton, R. Downer, B.J. Tyler, I.M. Stromberg, C.S. Mill, S.A. Penkett, B. Bandy, G.J. Dollard, T.J. Davies and B.M.R. Jones, 1991: Measurements of the entrainment of hydrogen peroxide into cloud system. *Atmos. Environ.*, **25A**, 2029–2038.
- Hellpointner, E. and S. Gäb, 1989: Detection of methyl, hydroxymethyl and hydroxyethyl hydroperoxides in air and precipitation. *Nature*, **337**, 631–634.
- Hewitt, C.N., G.L. Kok and R. Fall, 1990: Hydroperoxides in plants exposed to ozone mediate air pollution damage to alkene emitters. *Nature*, **344**, 56–58.
- Hewitt, C.N. and G.L. Kok, 1991: Formation and occurrence of organic hydroperoxides in the troposphere: laboratory and field observations. *J. Atmos. Chem.*, **12**, 181–194.
- Kleinman, L.I., 1986: Photochemical formation of peroxides in the boundary layer. *J. Geophys. Res.*, **91**, 10889–10904.
- Kleinman, L.I. and P.H. Daum, 1991: Oxidant limitation to formation of H_2SO_4 near a SO_2 source region. *Atmos. Environ.*, **25A**, 2023–2028.
- Lazrus, A.L., G.L. Kok, S.N. Gitlin, J.A. Lind and S. McLaren, 1985: Automated fluorometric method for hydrogen peroxide in atmospheric precipitation. *Anal. Chem.*, **57**, 917–922.
- Lind, J.A., A.L. Lazrus and G.L. Kok, 1987: Aqueous phase oxidation of sulfur (IV) by hydrogen peroxide, methylhydroperoxide and peroxyacetic acid. *J. Geophys. Res.*, **92**, 4171–4177.
- Martin, L.R. and D.E. Damschen, 1981: Aqueous oxidation of sulfur dioxide by hydrogen peroxide at low pH. *Atmos. Environ.*, **15**, 1615–1621.
- Masuch, G., A. Kettrup, R.J. Mallant and J. Slanina, 1986: Effects of H_2O_2 containing acidic fog on young trees. *Int. J. Environ. Anal. Chem.*, **27**, 183–213.
- Meagher, J.F., K.J. Olszyna, F.P. Weatherford and V.A. Mohnen, 1990: The availability of H_2O_2 and O_3 for aqueous phase oxidation of SO_2 . The question of linearity. *Atmos. Environ.*, **24A**, 1825–1829.
- Minami, Y. and Y. Ishizaka, 1995: Evolution of chemical composition in fog water near the summit of the high mountain in Japan. (submitted to *Atmos. Environ.*)
- Mohnen, V.A. and J.A. Kadlecsek, 1989: Cloud chemistry research at Whiteface Mountain. *Tellus*, **41**, 79–91.
- Okita, T., 1968: Concentration of sulfate and other inorganic materials in fog and cloud water and in aerosol. *J. Meteor. Soc. Japan*, **46**, 120–127.
- Olszyna, K.J., J.F. Meagher and E.M. Bailey, 1988: Gas-phase, cloud and rain-water measurements of hydrogen peroxide at a high-elevation site *Atmos. Environ.*, **22**, 1699–1706.
- Prinz B., 1987: Major hypothesis and factors—causes of forest damage in Europe. *Environment*, **29**, 10–37.
- Qian, G.W., Y. Ishizaka, Y. Minami, Y. Kurahashi, B.I. Tjandradewi and C. Takenaka, 1992: Transformation of individual aerosol particles in acidic fog evolution. *J. Meteor. Soc. Japan*, **70**, 711–722.
- Ross, H.B., C. Johansson and C. Serves, 1992: Summertime diurnal variations of atmospheric peroxides and formaldehyde in Sweden. *J. Atmos. Chem.*, **14**, 411–423.
- Sakugawa, H. and I.R. Kaplan, 1987: Atmospheric H_2O_2 measurement: Comparison of cold trap method with impinger bubbling method. *Atmos. Environ.*, **21**, 1791–1798.
- Sakugawa, H. and I.R. Kaplan, 1989: H_2O_2 and O_3 in the atmosphere of Los Angeles and its vicinity: factors controlling their formation and their roles as oxidants of SO_2 . *J. Geophys. Res.*, **94**, 12957–12973.
- Sakugawa, H., W. Tsai, I.R. Kaplan and Y. Cohen, 1990: Factors controlling the photochemical generation of gaseous H_2O_2 in the Los Angeles atmosphere. *Geophys. Res. Lett.*, **17**, 93–96.
- Sakugawa, H. and I.R. Kaplan, 1993: Comparison of H_2O_2 and O_3 content in atmospheric samples in the San Bernardino Mountains, Southern California. *Atmos. Environ.*, **27**, 1509–1515.
- Saxena, V.K., R.E. Stogner, A.H. Hendler, T.P. Defelice, R.J.Y. Yeh and N.H. Lin, 1989: Monitoring the chemical climate of the Mt. Mitchell state park for evaluation of its impact on forest decline. *Tellus*, **41**, 92–109.
- Simonaitis, R., K.J. Olszyna and J.F. Meagher, 1991: Production of hydrogen peroxide and organic perox-

- ides in the gas phase reactions of ozone with natural alkenes. *Geophys. Res. Lett.*, **18**, 9–12.
- Van Valin, C.C., J.D. Ray, J.F. Boatman and R.L. Gunter, 1987: Hydrogen peroxide in the air during winter over the south-central United States. *Geophys. Res. Lett.*, **14**, 1146–1149.
- Watanabe, K. and H. Tanaka, 1995: Measurement of gaseous hydrogen peroxide (H_2O_2) concentrations in the urban atmosphere. *J. Meteor. Soc. Japan*, **73**, 839–847.

乗鞍岳山頂付近における大気中の過酸化水素濃度の測定

渡辺幸一・石坂 隆・田中 浩

(名古屋大学大気水圏科学研究所)

大気中における過酸化水素や他の微量気体 (O_3 , SO_2) の濃度の測定を夏から初秋にかけて、中部日本に位置する乗鞍岳の山頂付近 (標高 2770 m) で行った。過酸化水素 (H_2O_2) やオゾン濃度は真夜中に濃度が最も高くなり、真昼に最も低くなった。深夜に H_2O_2 や O_3 濃度が高くなるのは上層大気の沈降によるものと考えられ、このような日変化は低地での変動とまったく逆である。また、夏の乗鞍岳では、 $\text{SO}_2(\text{S(IV)})$ を $\text{H}_2\text{SO}_4(\text{S(VI)})$ へと酸化させる能力の指標とされている $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ の比がほとんどの期間で 1 より大きく、 SO_2 の酸化剤が十分に存在していることがわかった。すなわち、夏期においては、水滴中での SO_2 の不均質酸化が非常に速いものと考えられる。