Bulletin of Glaciological Research 22 (2005) *51-55*

Measurements of peroxide concentrations in precipitation in Toyama and in the snow pit at Murododaira, near the summit of Mt. Tateyama

Koichi WATANABE, Ayumi IWAI, Nozomi TAKEDA and Yusaku TAKEBE
Department of Environmental Systems Engineering, Colleges of Technology,
Toyama Prefectural University, Kosugi-machi, Toyama 939-0398, Japan

(Received September 8, 2004; Revised manuscript received November 8, 2004)

Abstract

Measurements of the peroxide concentrations in precipitation were conducted at Kosugi-machi in Toyama from June 2002 to January 2004 and in the snow pit at Murododaira, near the summit of Mt. Tateyama, in April 2004. The concentrations of peroxides in the precipitation samples at Kosugi-machi exhibited a range from below the level of detection ($<0.1\mu$M) to 67μM. The peroxides concentrations were much higher from summer to early autumn than those from late autumn to early spring. The concentrations of peroxides in the snow pit at Murododaira ranged from below the level of detection to 2.6μM. The level of peroxides decreased with depth. Post-depositional loss of peroxides might have occurred.

1. Introduction

Hydrogen peroxide (H_2O_2) is considered to be an important oxidant of SO_2 (S(IV)) in atmospheric liquid water. Hydrogen peroxide has been found to be highly soluble in cloud and fog droplets or aqueous aerosols (Yoshizumi *et al.*, 1984; Watanabe *et al.*, 1996). The reaction between H_2O_2 and S(IV) in water droplets is very rapid and independent of the pH. The reaction between O_3 and S(IV), on the other hand, does not occur under conditions below pH 5 (Martin and Damschen, 1981). Organic hydroperoxides (ROOH) are thought to play an important role in the oxidation of S (IV), as well as H_2O_2 (Lind *et al.*, 1987). Therefore, the concentration of total peroxides (H_2O_2+ROOH) in the aqueous phase is a useful indicator of the oxidation capacity. Moreover, peroxides, as well as O_3, may contribute to vegetation damage (Hewitt and Terry, 1992). Peroxide concentrations are mainly dependent on the meteorological conditions (UV radiation, temperature and humidity) and the concentrations of atmospheric pollutants (Sakugawa *et al.*, 1990). Large seasonal variations in the concentrations of peroxide in the atmosphere have been observed (Sakugawa and Kaplan, 1989; Watanabe and Tanaka, 1995).

Peroxide concentrations in precipitation and cloud water have been measured, especially, in the United States and Europe (Olszyna *et al.*, 1988; Gunz and Hoffmann, 1990). Preliminary studies on peroxide in rain and cloud water in central parts of Japan have been reported (Watanabe *et al.*, 1999; 2001a; 2001b). However, there is a shortage of such data on peroxides in East Asian countries. Long-term peroxide data were not obtained in Japan. Peroxide concentrations have also been measured in polar snow samples (Neftel *et al.*, 1984; 1995; Kamiyama and Nakayama, 1992; Kamiyama *et al.*, 1996; Watanabe *et al.*, 1998). Measurements of peroxides in an ice core may be useful for understanding past atmospheric oxidation (Neftel *et al.*, 1984). In discussing peroxides in the past from ice core analysis, it is necessary to consider the transfer processes in the air to snow and post-depositional modification (Neftel *et al.*, 1995). The post-depositional loss of peroxides also was observed in the snow pits in the polar regions (Motoyama *et al.*, 2001). Snow is several meters deep in the high mountains of Japan. However, measurements of peroxides in snow at high elevations have not been made in Japan.

In this paper, the concentrations of peroxides in precipitation, including snow fall in Toyama and in the snow pit at Murododaira, near the summit of Mt. Tateyama in Japan, are presented, and the characteristics of peroxide concentrations are examined.

2. Methods

Precipitation samples were collected by a 1000 ml Teflon bottle (100 mm ID) on the roof of the building of the college of Technology, Toyama Prefectural University at Kosugi-machi, in Toyama, from June 2002 to January 2004. Figure 1 is a map of Japan showing

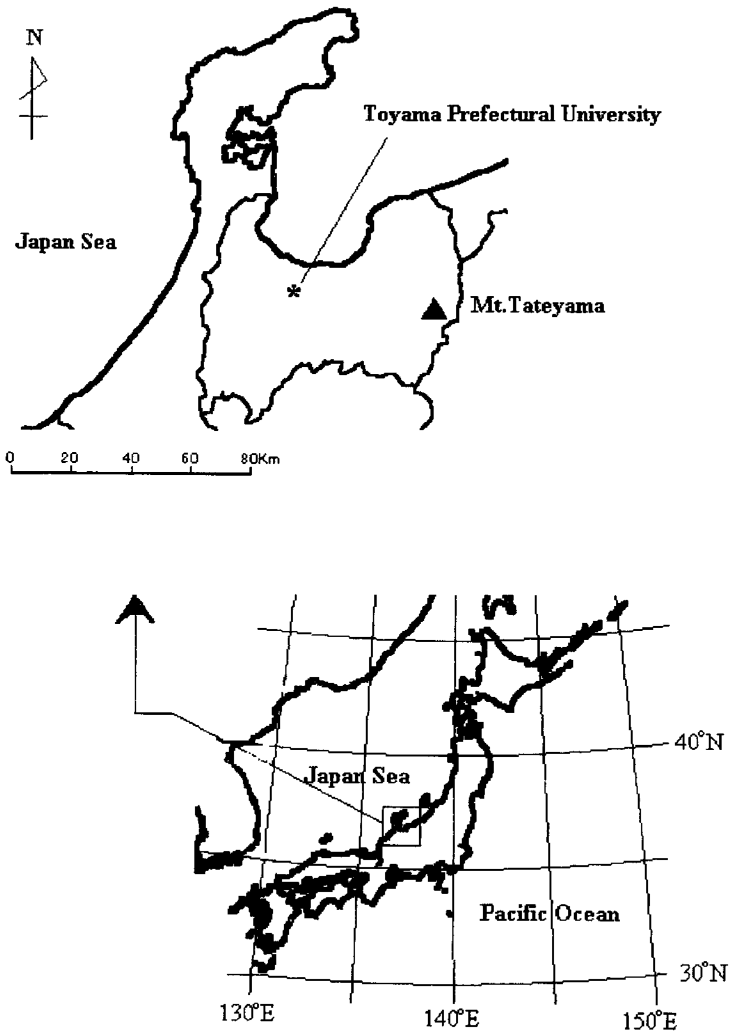

Fig. 1. Map of Japan showing the locations of Toyama Prefectural University and Mt. Tateyama.

the locations of Toyama Prefectural University and Mt. Tateyama. The precipitation sampling was usually performed in the early afternoon when gaseous peroxide is usually high (Sakugawa and Kaplan, 1989; Watanabe and Tanaka, 1995). Sampling time was within 3 hours. The concentrations of peroxides in rainwater were measured immediately after collection. Snowfall samples were melted at room temperature and immediately analyzed.

The snow pit study was performed at Murododaira (36.6°N, 137.6°E, 2450 m altitude), near the summit of Mt. Tateyama (Fig. 1), on 24–25 April 2004. The snow cover at Murododaira was about 6 m deep. The sampling interval for analysis was about 10 cm. The snow samples were transported to Toyama Prefectural University on 25 April and preserved in a freezer (−10℃). The measurements of peroxides were performed within one week. The preliminary snow pit study for peroxide measurements at Murododaira was made on 20–21 April in 2003. Snow samples from the pit wall were taken from the top to a depth of 1.5 m depth. Peroxide concentrations also were measured within one week.

Peroxide concentrations were measured by the fluorometric method, using *p*-hydroxyphenyl acetic acid and peroxidase reagents (Lazrus *et al.*, 1985; Kamiyama and Nakayama, 1992), as described in detail by Watanabe *et al.* (1995). The fluorescence reagents, 1 ml *p*-hydroxyphenyl acetic acid (1.5×10^{-2} M) in a phosphate buffer (adjusted to pH 7) and 1ml peroxidase (50 unit ml^{-1}) in a phosphate buffer (adjusted to pH 7), were added to the 1 ml liquid sample. Several minutes later, 1 ml NaOH (1 N) was added to stabilize the generated fluorescence. The amount of fluorescence in the solution was determined by a fluorescence spectrophotometer (Hitachi Corporation, Model F-2500). This method determines the concentration of total peroxides (H_2O_2+ROOH). To discriminate H_2O_2 from ROOH, catalase regent has been used (Lazrus *et al.*, 1985; Watanabe *et al.*, 1995). ROOH are also important oxidants of S(IV), therefore we measured only total peroxides. To calibrate, a standard H_2O_2 solution was made from a stock solution that was titrated with a standard $KMnO_4$ solution.

The pH and electric conductivity (EC) in the sampling solution were measured with a pH meter and an

Table 1. Summary of the concentrations of peroxides in precipitation at Kosugi-machi, Toyama. BDL denotes values below the detection limit ($<0.1\mu M$).

Date	Precipitation form	Peroxides (μM)
14 June 2002	Rain	41
10 July 2002	Rain	27
15 October 2002	Rain	6.2
8 November 2002	Rain	BDL
13 November 2002	Rain	0.20
27 November 2002	Rain, Snow	BDL
5 March 2003	Snow	0.43
5 April 2003	Rain	BDL
20 April 2003	Rain	22
13 June 2003	Rain	50
20 June 2003	Rain	67
1 September 2003	Rain	31
24 September 2003	Rain	60
23 October 2003	Rain	1.0
20 November 2003	Rain	BDL
12 December 2003	Rain	BDL
14 January 2004	Snow	BDL

EC meter, respectively. Unfortunately we could not measure the pH and EC in the precipitation samples at Kosugi-machi. The pH and EC were measured only snow pit samples at Mt. Tateyama.

3. Results and discussion

3.1. *Peroxide concentrations in precipitation in Toyama*

A summary of the measured peroxide concentrations in precipitation (rainwater and snowfall) at Kosugi-machi, Toyama, from June 2002 to January 2004 is shown in Table 1. The concentrations of peroxides exhibited a range from below the level of detection ($<0.1\mu M$) to $67\mu M$. The concentrations of chemical constituents seem to be affected by an amount of precipitation. Unfortunately, the amounts of precipitation could not be measured. The level of peroxides was lower than that in cloud water at high elevations in Japan. For example, peroxide concentrations in fog water near the summit of Mt. Norikura were 3-180μM in summer (Watanabe *et al.*, 1999). Chemical constituents are usually condensed in cloud water.

There were strong seasonal variations. The concentrations of peroxides from the summer to the early autumn were much higher than those from the late autumn to the early spring. Similar seasonal variations of peroxides have also been measured in the gas phase (Sakugawa and Kaplan, 1989; Watanabe and Tanaka, 1995). Peroxides are mainly produced by photochemical reactions (Sakugawa *et al.*, 1990); therefore, the formation of peroxides in the atmosphere is accelerated during the summer season. As mentioned above, peroxides are important oxidants for SO_2. The capacity of SO_2 oxidation seems to be much lower in winter than in summer. There may be a condition $[H_2O_2]<[SO_2]$ (*Oxidant Limitation*) in the atmosphere during the cold months. The concentrations of peroxides in most of the precipitation samples were below detection limit in the cold seasons. Peroxides might have been consumed by SO_2 in the atmospheric droplets, especially in winter.

3.2. *Peroxide concentrations in the snow pit at Murododaira*

Ranges in peroxides concentrations, pH and EC in the snow pit at Murododaira are presented in Table 2. The concentrations of peroxides ranged from below the level of detection to $2.6\mu M$. A vertical profile of the peroxide concentrations in the snow pit in April 2004 is shown in Fig. 2. The snow stratigraphy and profiles of pH and EC are also presented. The ranges in pH and EC were from 4.6 to 5.5 and from 2 to $22\mu S/cm$, respectively. There was a weak relationship between the peroxide concentrations and the pH. A weak negative correlation between the peroxides and the EC also was seen. The highest concentrations of peroxides were seen at the top of the snow layer which was composed of new snow. The levels of peroxides de-

Table 2. Ranges in peroxide concentrations, pH, and EC in the snow pits at Murododaira on 20-21 April 2003 and 24-25 April 2004. N and BDL denote the number of samples and values below the detection limit (<0.1μM), respectively.

Date	Sampling snow layers	N	Peroxides (μM)	pH	EC (μS/cm)
20-21 April 2003	0～1.5 m depth	16	0.21～2.0	4.9～5.6	4～45
24-25 April 2004	0～6.0 m depth	59	BDL～2.6	4.6～5.5	2～22

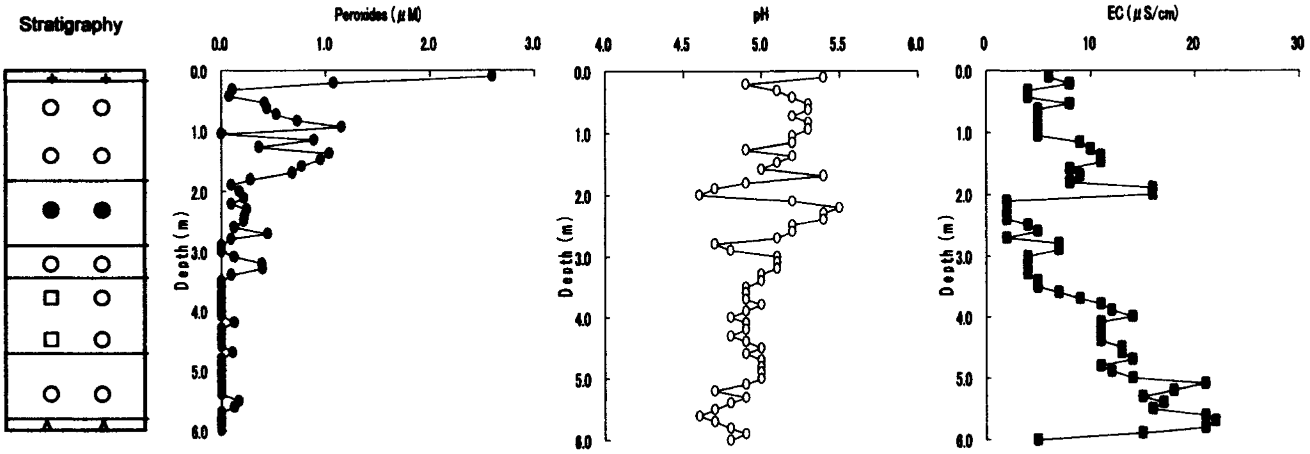

Fig. 2. Snow stratigraphy and vertical profiles of peroxide concentrations, pH, and EC in the snow pit at Murododaira, near the summit of Mt. Tateyama, on 24-25 April 2004.

creased with depth. The concentrations were below the detection limit in most of the samples below 4 m (Fig. 2). The snow at the lower layers was deposited, when the photochemical formation of peroxides is suppressed. A low level of peroxides might have been found in the deposited snowfall; in addition, post-depositional loss of peroxides seemed to occur, in particular, in the lower layers. However, details of the mechanism for the loss of peroxides in the snow pit are not available at this point.

There are comparable peroxide data in the snow pit in polar regions. The peroxides concentrations at Murododaira were lower than those in snow samples from the pit wall at NGRIP, Greenland (Motoyama *et al.*, 2001). Sigg *et al.* (1992) reported that a high concentration of H_2O_2 in the air was observed during summer at Summit, Greenland and the H_2O_2 concentration in fresh snow samples was around 20μM. Relatively high concentrations of H_2O_2 were detected in the snow layers deposited during summer and autumn in Greenland (Motoyama *et al.*, 2001). The concentrations of peroxides at Murododaira were similar to those in the snow pits in Svalbard (Motoyama *et al.*, 2001). The H_2O_2 in Svalbard was changed by perocolation of snowmelt water after accumulation. Peroxides at Murododaira might have also been modified by snowmelt.

Peroxide concentrations may be higher in rainwater than in snowfall. We simultaneously collected rainwater at Kosugi-machi and snowfall at Murododaira on 20 April in 2003. Peroxide concentrations in the atmosphere are usually large at high altitude (Kleinman and Daum, 1991; Watanabe *et al.*, 1995). However, the concentrations of peroxides were 1.0μM at Murododaira but 22μM at Kosugi-machi (Table 1). The main component of peroxides seems to be H_2O_2. Scavenging processes of H_2O_2 from atmosphere may be different in rainwater and snowfall. According to Sigg *et al.* (1992), the diffusional growth of snow is an important process of H_2O_2 scavenging. There is no fractionation between H_2O_2 and H_2O during diffusional growth. On the other hand, H_2O_2 may be preferentially absorbed by rain droplets because of the high solubility of H_2O_2, for which Henry's law constant is high. The Henry's law constant is given by Lind and Kok (1986) as follows:

$$H(T)=\exp(A/T-B),$$

where $H(T)$ is Henry's law constant ($\mathrm{Matm^{-1}}$), T is the ambient temperature (K), $A=6621$ and $B=11$. When the ambient temperature is 10℃, the Henry's law constant is about 2.4×10^5 ($\mathrm{Matm^{-1}}$).

Acknowledgments

The authors thank Profs. K. Kawada, H. Satake, K. Suzuki and T. Iida, Drs. M. Igarashi and S. Matoba, K. Kawashima and C. Natori, and the members of Toyama University, Nagoya University, Sinsyu University, and the subcommittee of snow and ice chemistry for their support of the snow pit study at Mt. Tateyama. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (No. 16710011).

References

Gunz, D. W. and Hoffmann, M. R. (1990): Atmospheric chemistry of peroxides: a review. Atmos. Environ., **24A**, 1601-1633.

Hewitt, C. N. and Terry, G. (1992): Understanding ozone plant chemistry. Envir. Sci. Technol., **26**, 1891-1892.

Kamiyama, K. and Nakayama, E. (1992): Determination of hydrogen peroxide in snow, preliminary results for snow samples in the inland region, Antarctica. Proc. NIPR Symp. Polar Meteor. Galaciol., **5**, 113-119.

Kamiyama, K., Motoyama, H., Fujii, Y. and Watanabe, O. (1996): Distribution of hydrogen peroxide in surface snow over Antarctic ice sheet. Atmos. Environ., **30**, 967-972.

Kleiman, L. I. and Daum, P. H. (1991): Oxidant limitation to formation of H_2SO_4 near a SO_2 source region. Atmos. Environ., **25A**, 2023-2028.

Lazrus, A. L., Kok, G. L., Gitlin, S. N., Lind, J. A. and Mclaren, S. (1985): Automated fluorometric method for hydrogen peroxide in atmospheric precipitation. Anal. Chem., **57**, 917-922.

Lind, J. A. and Kok, G. L. (1986): Henry's law determination for aqueous solutions of hydrogen peroxide, methylhydroperoxide and peroxyacetic acid. J. Geophys. Res., **91**, 7889-7895.

Lind, J. A., Lazrus, A. L. and Kok, G. L. (1987): Aqueous phase oxidation of sulfur (IV) by hydrogen peroxide, methylhydroperoxide and peroxyacetic acid. J. Geophys. Res., **92**, 4171-4177.

Martin, L. R. and Damschen, D. E. (1981): Aqueous oxidation of sulfur dioxide by hydrogen peroxide at low pH. Atmos. Environ., **15**, 1615-1621.

Motoyama, H., Watanabe, O., Kamiyama, K., Igarashi, M., Goto-Azuma, K., Fujii, Y., Iizuka, Y., Matoba, S., Narita, H. and Kameda, T. (2001): Regional characteristics of chemical constituents in surface snow, Arctic cryosphere. Polar Meteor. Glaciol., **15**, 55-66.

Neftel, A., Jacob, P. and Klockow, D. (1984): Measurements of hydrogen peroxide in polar ice samples. Nature, **311**, 43-45.

Neftel, A., Bales, R. C. and Jacob, D. J. (1995): H_2O_2 and HCHO in polar snow and their relation to atmospheric chemistry. In Ice Core Studies of Biogechemical Cycles, NATO ASI Series, edited by R. Delmas, 249-264.

Olszyna, K. J., Meagher, J. F. and Bailey, E. M. (1988): Gas-phase, cloud and rain-water measurements of hydrogen peroxide at high-elevation site. Atmos. Environ., **22**, 1699-1706.

Sakugawa, H. and Kaplan, I. R. (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., Tsai, W., Kaplan, I. R. and Cohen, Y. (1990): Factors controlling the photochemical generation of gaseous H_2O_2 in the Los Angeles atmosphere. Geophys. Res. Lett., **17**, 93-96.

Sigg, A., Staffelbach, T. and Neftel, A. (1992): Gas phase measurements of hydrogen peroxide in Greenland and their meaning for the interpretation of H_2O_2 records in ice cores. J. Atmos. Chem., **14**, 223-232.

Watanabe, K. and Tanaka, H. (1995): Measurement of gaseous hydrogen peroxide (H_2O_2) concentrations in the urban atmosphere. J. Meteor. Soc. Japan, **73**, 839-847.

Watanabe, K., Ishizaka, Y. and Tanaka, H. (1995): Measurements of atmospheric peroxides concentrations near the summit of Mt. Norikura in Japan. J. Meteor. Soc. Japan, **73**, 1153-1160.

Watanabe, K., Nagao, I. and Tanaka, H. (1996): Atmospheric hydrogen peroxide concentration measured at Ogasawara Hahajima Island in the sub-tropical Pacific Ocean. J. Meteor. Soc. Japan, **74**, 393-398.

Watanabe, K., Kamiyama, K., Watanabe, O. and Satow, K. (1998): Evidence for an 11-year cycle of atmospheric H_2O_2 fluctuation recorded in an ice core at the coastal region, East Antarctica. J. Meteor. Soc. Japan, **76**, 447-451.

Watanabe, K., Ishizaka, Y. and Takenaka, C. (1999): Chemical composition of fog water near the summit of Mt. Norikura in Japan. J. Meteor. Soc. Japan, **77**, 997-1006.

Watanabe, K., Ishizaka, Y. and Takenaka, C. (2001a): Chemical characteristics of cloud water over the Japan Sea and the Northwestern Pacific Ocean near the central part of Japan: airborne measurements. Atmos. Environ., **35**, 645-655.

Watanabe, K., Ishizaka, Y., Minami, Y. and Yoshida, K. (2001b): Peroxide concentrations in fog water at mountainous sites in Japan. Water Air and Soil Pollution, **130**, 1559-1564.

Yoshizumi, K., Aoki, K., Nouchi, I., Kobayashi, T., Kamakura, S. and Tajima, M. (1984): Measurements of the concentration in rainwater and of the Henry's law constant of hydrogen peroxide. Atmos. Environ., **18**, 395-401.