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 μM) to 67 μM. 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 2.6 μM. The level of peroxides decreased with depth. Post-depositional loss of peroxides might have occurred.

1. Introduction

Hydrogen peroxide (H₂O₂) is considered to be an important oxidant of SO₂ (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 H₂O₂ and S(IV) in water droplets is very rapid and independent of the pH. The reaction between O₃ and S(IV), on the other hand, does not occur under conditions below pH 5 (Martin and Danshen, 1981). Organic hydroperoxides (ROOH) are thought to play an important role in the oxidation of S (IV), as well as H₂O₂ (Lind et al., 1987). Therefore, the concentration of total peroxides (H₂O₂ + ROOH) in the aqueous phase is a useful indicator of the oxidation capacity. Moreover, peroxides, as well as O₃, 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., 1999). Large seasonal variations in the concentrations of peroxide in the atmosphere have been observed (Sakugawa and Kaplan, 1988; 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 (Nefel 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 (Nefel 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 (Nefel 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
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°C). 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 (Lazarus 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 1 ml 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 (H2O2 + ROOH). To discriminate H2O2 from ROOH, catalase reagent has been used (Lazarus et al., 1985; Watanabe et al., 1995). ROOH are also important oxidants of Si(IV), therefore we measured only total peroxides. To calibrate, a standard H2O2 solution was made from a stock solution that was titrated with a standard K2MnO4 solution.

The pH and electric conductivity (EC) in the sampling solution were measured with a pH meter and an
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 μM) to 67 μM. 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 3-180 μM 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 SO₂. The capacity of SO₂ oxidation seems to be much lower in winter than in summer. There may be a condition \[
\text{[H}_2\text{O}_2\text{]} < \text{[SO}_2\text{]} \]
(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 SO₂ in the atmospheric droplets, especially in winter.

3.2. Peroxide concentrations in the snow pit at Murodoaira

Ranges in peroxides concentrations, pH and EC in the snow pit at Murodoaira are presented in Table 2. The concentrations of peroxides ranged from below the level of detection to 2.6 μM. 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 μS/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.

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

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 H₂O₂ in the air was observed during summer at Summit, Greenland and the H₂O₂ concentration in fresh snow samples was around 20 µM. Relatively high concentrations of H₂O₂ 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 H₂O₂ in Svalbard was changed by percolation 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 1.0 µM at Murododaira but 22 µM at Kosugi-machi (Table 1). The main component of peroxides seems to be H₂O₂. Scavenging processes of H₂O₂ 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 H₂O₂ scavenging. There is no fractionation between H₂O₂ and H₂O during diffusional growth. On the other hand, H₂O₂ may be preferentially absorbed by rain droplets because of the high solubility of H₂O₂, 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 (Matm⁻¹), T is the ambient temperature (K), A = 6621 and B = 11. When the ambient temperature is 10°C, the Henry's law constant is about 2.4×10⁶ (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 Univer-
in polar snow and their relation to atmospheric chemistry. In Ice Core Studies of Biogeochemical Cycles, NATO ASI Series, edited by R. Delmas, 249–284.


