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Measurements of peroxide concentrations in precipitation and dew water in Toyama, Japan

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Abstract

Measurements of the peroxide concentrations in precipitation were conducted in Imizu City, Toyama Prefecture, Japan, from July 2005 to March 2009 and in dew water in the autumn of 2008. The peroxide concentrations in the precipitation samples exhibited a range from below the level of detection, $<0.1\mu$M, to 190μM with strong seasonal variations. The peroxide concentrations during the winter were higher in rainwater than in the snow, perhaps because rain and snow have different processes of scavenging peroxides from the atmosphere. The concentrations of peroxides in dew water in Imizu City ranged from 0.8 to 3.6μM from September to November in 2008. At lower sites, the peroxide concentrations were significantly lower in dew water than in rainwater, however, higher concentrations in dew water, 65μM, were detected at Murododaira (2450 m a.s.l.), near the summit of Mt. Tateyama.

1. Introduction

Hydrogen peroxide, H_2O_2, considered an important oxidant of SO_2, S(IV), in atmospheric liquid water, has been found to be highly soluble in cloud and fog droplets or aqueous aerosols (Watanabe *et al.,* 1996). The reaction between H_2O_2 and S(IV) in water droplets is very rapid and is 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 that of 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 oxidation capacity. Moreover, peroxides, as well as O_3, may contribute to vegetation damage (Hewitt and Terry, 1992; Kume *et al.,* 2001). Peroxide concentrations are mainly dependent on the meteorological conditions, *e.g.* UV radiation, temperature and humidity, and the concentrations of atmospheric pollutants (Sakugawa *et al.,* 1990). Large seasonal variations in the concentrations of peroxides 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 (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; 2005; 2006). However, there is still a shortage of such data on peroxides in East Asian countries. Up to now, no long-term observation of peroxides has been performed in Japan. Moreover, peroxide concentrations have rarely been measured in dew water. Recently, O_3 concentrations in the background troposphere have significantly increased over East Asian countries, including Japan (Akimoto *et al.,* 1994). The increase in O_3 may accelerate the formation of peroxides in the atmosphere; therefore, measurements of peroxides are important to estimate environmental conditions.

In this paper, the concentrations of peroxides in precipitation, including snowfall and dew water in Toyama, Japan and the characteristics of peroxide concentrations are examined. The preliminary results of peroxide measurement in dew water near the summit of Mt. Tateyama are also discussed.

2. Methods

Sampling of precipitation (rain and snow) and dew water was performed on the roof of the building (20 m above the ground level) at the College of Technology, Toyama Prefectural University (15 m a.s.l.) in Imizu City, Toyama, Japan. Precipitation samples were collected in a 1000 ml Teflon bottle (100 mm ID) from July 2005 to March 2009. Unfortunately, precipitation could not be collected from March to October in 2006. In the autumn of 2008, dew water was sampled during the nighttime on a 1 m^2 Teflon sheet on foaming polystyrene. Dew water was also collected at Murododaira (2450 m a.s.l.), near the summit of Mt. Tateyama, at 0–3 H JST on 12 September, 2008. The sampling times for precipitation and dew water collection were usually within 4 hours. The peroxide concentrations in rainwater and dew water were measured immediately after collection. Snow samples were melted at room temperature and immediately analyzed. Figure 1 is a map of Japan showing the locations of Toyama Prefectural University and Mt. Tateyama. In this paper, the sampling sites, Toyama Prefectural University and Murododaira, Mt. Tateyama, are described as Imizu City and Murododaira, respectively.

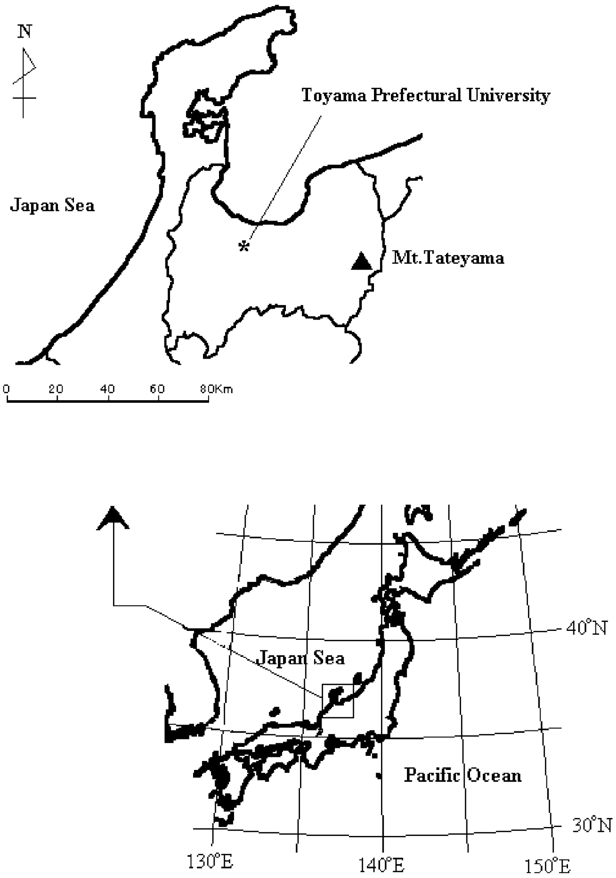

Fig. 1. Map showing the locations of Toyama Prefectural University, Imizu City, and Mt. Tateyama in Toyama, Japan.

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.* (2005). We also determined individual peroxides using HPLC separation (Kok *et al.,* 1995). The concentrations of organic hydroperoxides, such as methylhydroperoxide (MHP), were less than 5% of total peroxide concentrations (Watanabe, unpublished data). Therefore, H_2O_2 is considered a main component of peroxides in this study.

3. Results and discussion

3.1 Peroxide concentrations in precipitation

A summary of the concentrations of peroxides in precipitation in Imizu City from July 2005 to March 2009 is shown in Table 1. The peroxide concentrations ranged from below the level of detection, $<0.1\mu M$, to $190\mu M$, and the concentrations were significantly higher from May to October than from November to April. Time series of the peroxide concentrations are presented in Fig. 2. The concentrations of chemical constituents seemed to be affected by the amounts of precipitation, which, unfortunately, could not be measured. High peroxide concentrations, $>100\mu M$, which may result in serious damage to vegetation (Kume *et al.,* 2001), were sometimes observed, indicating that background concentrations of peroxides may be increasing in the troposphere over Japan.

The peroxide concentrations in Imizu City from 2005 to 2009 are plotted for each month in Fig. 3. There were strong seasonal variations in peroxide concentrations. From summer to early autumn, the peroxide concentrations were much higher than those from late autumn to spring (Table 1). As mentioned above, peroxides are important SO_2 oxidants. The capacity for in which 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 season. Similar seasonal variations in 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. However, peroxide concentrations in precipitation may be dependent on not only gaseous peroxide concentrations but also scavenging processes from the atmosphere.

The peroxide concentrations in the rain and snow in Imizu City during the winter months are shown in Fig. 4. Peroxide concentrations were usually higher in rain than in snow, and relatively high concentrations of peroxides were detected in rainwater. The scavenging processes of H_2O_2, the main component of

Table 1. Summary of the peroxide concentrations in the precipitation in Imizu City from July 2005 to March 2009. N and BDL denote the number of samples and values below the detection limit, $<0.1 \mu$M, respectively.

Period	N	Mean (μM)	Minimum (μM)	Maximum (μM)
Jan. – Dec.	113	16	BDL	190
May – Oct.	38	45	0.8	190
Nov. – Apr.	75	1.7	BDL	17

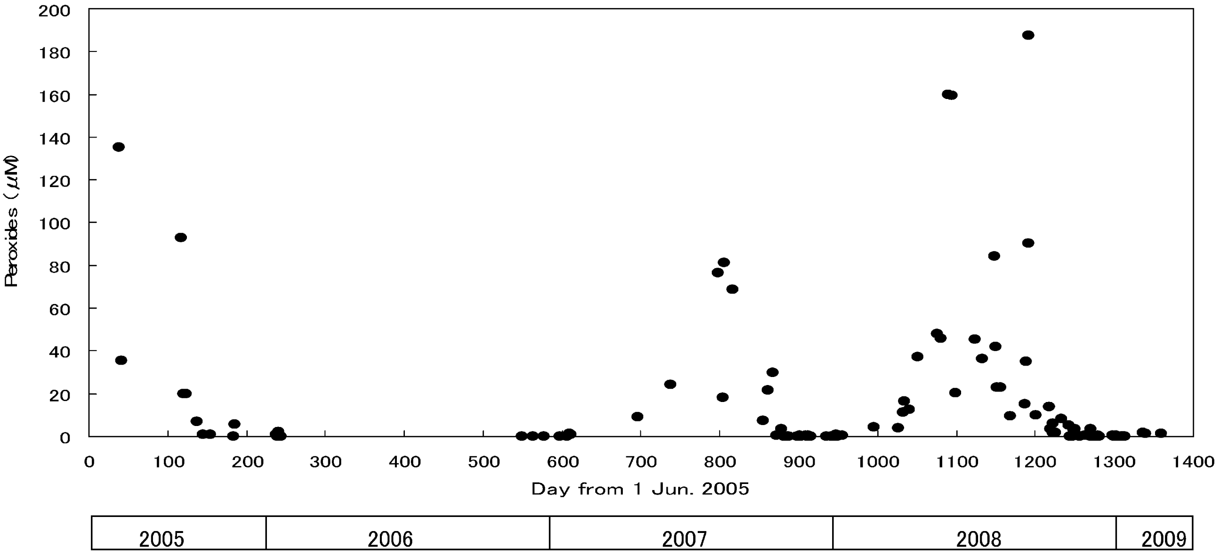

Fig. 2. Time series of the peroxide concentrations in precipitation in Imizu City from 2005 to 2009. Measurements of peroxides in precipitation could not be performed from March to October in 2006.

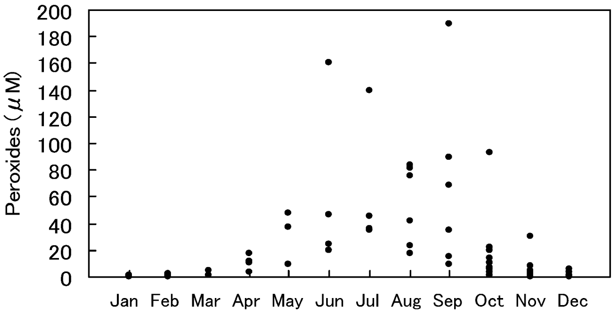

Fig. 3. Seasonal variations of the peroxide concentrations in precipitation in Imizu City. The peroxide concentrations from 2005 to 2009 are plotted for each month.

peroxides, from the atmosphere may differ between rain and snow. Watanabe *et al.* (2005) reported that the concentrations of peroxides were much higher in rainwater in Imizu City than in snowfall at Murododaira in April 2003.According to Sigg *et al.* (1992), the diffusional growth of snow is an important process in 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

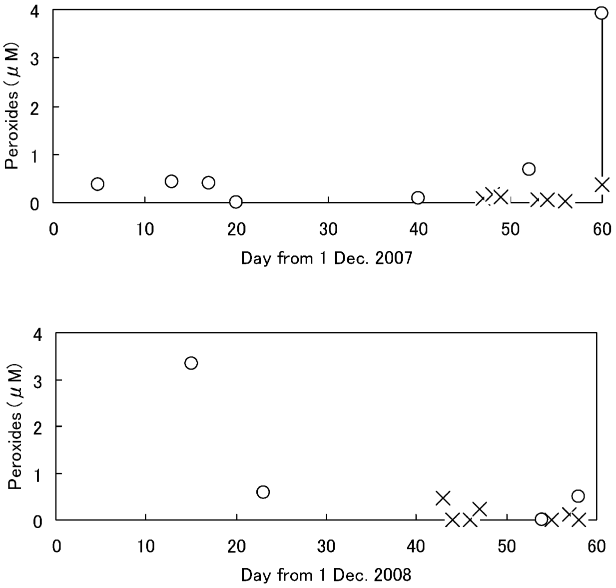

Fig. 4. The peroxide concentrations in rain (○) and snow (×) in Imizu City from December 2007 to January 2008 (upper panel) and December 2008 to January 2009 (lower panel).

rain droplets because of the high solubility of H_2O_2, for which Henry's law constant is high. 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 (M atm^{-1}), T is the ambient temperature (K), $A=6621$ and $B=11$. When the ambient temperature is 10℃, Henry's law constant is about 2.4×10^5 (M atm^{-1}). Similar phenomena were observed at Murododaira in a snow pit in which relatively high peroxide concentrations were sometimes detected in the granular snow layers (Watanabe *et al.,* 2005; 2008). Granular snow is formed by the percolation of snowmelt water or rainwater, and peroxides might have dissolved in the surface snowmelt water.

3.2 Peroxide concentrations in dew water

A summary of the measured peroxide concentrations in dew water in Imizu City and at Murododaira in the autumn of 2008 is shown in Table 2. The concentrations of peroxides in the dew water sampled in Imizu City were 0.8–3.6 μM. The peroxide concentrations in the dew water in Imizu City were the same as the H_2O_2 concentrations in dew water in Higashi-Hiroshima City, where Sakugawa *et al.* (2006) reported that the peroxide concentrations ranged from below the level of detection to 3.5 μM from April 1997 to December 1998. The peroxide concentrations may be significantly lower in dew water than in rainwater at lower sites. The highest concentrations, 65 μM in the dew water, were detected at Murododaira (Table 2).

Dew water is usually seen under calm conditions in the nighttime and absorbs soluble gases, such as peroxides, in the ambient air. Gaseous peroxide concentrations are very low from nighttime to early morning at low-altitude sites (Sakugawa and Kaplan, 1989; Watanabe and Tanaka, 1995). When the wind speed is low and a boundary layer is developed, peroxide concentrations decrease rapidly after sunset (Watanabe and Tanaka, 1995). As a result, the concentrations of peroxides in dew water may be low. On the other hand, peroxide concentrations at high mountainous sites in the air are higher in the nighttime than in the daytime (Watanabe *et al.,* 1995). It is natural that peroxides in dew water were much higher at Murododaira than in Imizu City. Kume *et al.* (2001) reported that high concentrations of H_2O_2 in dew water resulted in serious damage to vegetation and that OH radicals formed by Fenton's reaction of H_2O_2 in the liquid phase after sunrise could damage vegetation. To evaluate the effects of peroxides on high-altitude ecosystems, further measurements of peroxides in dew water at mountainous sites such as Murododaira are required.

Table 2. Summary of the concentrations of peroxides in dew water in Imizu City and at Murododaira.

Date (Site)	Peroxides (μM)
12 Sep. 2008 (Murododaira)	65
23 Sep. 2008 (Imizu City)	3.6
16 Oct. 2008 (Imizu City)	2.1
30 Oct. 2008 (Imizu City)	1.6
6 Nov. 2008 (Imizu City)	1.3
13 Nov. 2008 (Imizu City)	0.8
27 Nov. 2008 (Imizu City)	1.1

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