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Measurements of atmospheric hydroperoxides over a rural site in central Japan during summers using a helicopter

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HIGHLIGHTS

- Concentrations of hydroperoxides as well as the concentrations of O_3, SO_2 and NO_X* in the high-altitude atmosphere were measured using a helicopter.
- Hydroperoxides in the high-altitude atmosphere were measured using an HPLC system in a laboratory within 5–10 min after sampling.
- The concentrations of hydroperoxides were highest in the atmosphere at altitudes of 6,000 to 8,000 ft.
- The potential capacity of SO_2 oxidation in the aqueous phase is large during summers over central Japan.

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ABSTRACT

The concentrations of hydroperoxides (H_2O_2 and MHP), O_3, SO_2 and NO_X* over Imizu City, Toyama Prefecture, Japan were measured during summers using a helicopter. The concentrations of hydroperoxides were analyzed by an HPLC system within 5–10 min after the sampling. The H_2O_2 concentration was lowest at the surface, and the highest concentration was detected at altitudes of 6000 and 8000 ft. The MHP was also higher in the high-altitude atmosphere. Significantly high concentrations of hydroperoxides were observed when air pollutants were transported from China. The concentration of H_2O_2 was higher than that of SO_2 above 4000 ft where the potential capacity of SO_2 oxidation in the aqueous phase is large. A helicopter is useful for measuring of hydroperoxides in the high-altitude atmosphere using an HPLC system in a laboratory.

1. Introduction

Hydroperoxides (hydrogen peroxide and organic hydroperoxides) play an important role in radical chemistry in the gas-phase and aqueous-phase chemistry of acidic precipitation. Hydroperoxides such as hydrogen peroxide (H_2O_2) and methyl hydroperoxide (CH_3OOH, MHP) are produced through the self-reaction of peroxy radicals that are intimately linked to ozone (O_3) chemistry (e.g. Jackson and Hewitt, 1999; Lee et al., 2000; Vione et al., 2003). Hydroperoxides also play significant roles in atmospheric processes, such as SO_2 oxidation in liquid water and the formation of secondary organic aerosol (SOA); they also damage vegetation (e.g. Möller, 1989, 2009; Watanabe et al., 1999; Kume et al., 2001; Hua et al., 2008; Chen et al., 2010; Herckes et al., 2013).

Recently, the O_3 concentration in the background troposphere has significantly changed over East Asian countries (Akimoto et al., 1994; Tanimoto, 2009). According to Tanimoto (2009), an increase of approximately 1 ppb per year in the average concentration of O_3 was observed from 1998 to 2006 over Japan, especially in the spring when the background O_3 shows maximum concentrations in the middle to high latitudes (Watanabe et al., 2005). The change in the O_3 concentration may significantly affect the formation of hydroperoxides. Measuring hydroperoxides in the atmosphere at high elevations is important for evaluating the oxidative capacity of SO_2 in cloud water and effects harmful to the ecosystem at mountainous sites. However, there has been a shortage of gaseous hydroperoxide data in the high-altitude atmosphere over East Asian countries including Japan (Watanabe et al., 1995; Ren et al., 2009). In particular, vertical profiles of hydroperoxides have hardly been measured over Japan.

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Hydroperoxides in the high-altitude atmosphere have been measured many times over the United States and Europe (e.g., Kleinman and Daum, 1991; O'Sullivan et al., 2004; Snow et al., 2007; Klippel et al., 2011). Airborne measurements have usually been made using a fixed-wing aircraft, such as a Cessna plane (e.g., Kleinman and Daum, 1991; Hatakeyama et al., 2001; Watanabe et al., 2001a; Matsuki et al., 2003; Klippel et al., 2011; Nair et al., 2012; Maki et al., 2013; Srivastava et al., 2013). Many hydroperoxide measurements, especially airborne measurements, have been made mainly by a wet chemical system based on the technique described by Lazrus et al. (1986), using identical chemistry (peroxidase-catalyzed dimerization of *p*-hydroxyphenylacetic acid with fluorometric detection). The instrument is equipped with two channels. One channel delivers total hydroperoxides (H_2O_2 + organic hydroperoxides) while, in the other channel, H_2O_2 is selectively decomposed by catalase (organic hydroperoxides are delivered). The H_2O_2 mixing ratio is estimated based on the difference between total hydroperoxides and organic hydroperoxides. It is important to check the catalase efficiency (Lazrus et al., 1985, 1986; Ayers et al., 1996; Lee et al., 2000; Klippel et al., 2011).

To measure H_2O_2 exactly, it is best to analyze hydroperoxides in sampling solution immediately after collection using a high-performance liquid chromatography (HPLC) system to separate the H_2O_2 and organic hydroperoxides such as MHP from the total hydroperoxides (Hatakeyama et al., 1993; Kok et al., 1995; Morgan and Jackson, 2002; Takami et al., 2003). Usually, it is difficult to load an HPLC system onto an observation airplane. Concentrations of hydroperoxides in the high-altitude atmosphere were measured using an HPLC system aboard large NASA airplanes, such as the DC-8 and P3-B aircrafts (O'Sullivan et al., 2004; Snow et al., 2007). However, such large aircrafts are difficult to charter and, thus, are not suitable for local observation. In this study, we used a helicopter to measure hydroperoxides in the high-altitude atmosphere. A helicopter seems to be useful for topical observation (e.g., Imhoff et al., 1995; Matsunaga et al., 2010; Siebert et al., 2010).

The aim of this paper is to present a new method of measuring hydroperoxide in the high-altitude atmosphere using helicopter and an HPLC system in a laboratory. We report the preliminary results of observations during summers and discuss the behaviors of hydroperoxides and the potential capacity for the oxidation of SO_2 over a rural site near the coast of the Japan Sea, where a large amount of air pollution is transported from Asia as well as from industrial regions in Japan.

2. Observation

2.1. Observation site

A helicopter was used for observation over Imizu City, where Toyama Prefectural University (16 m above sea level) is located, on a rural site in Toyama Prefecture, Japan (Fig. 1) during summers (or early autumns) from 2010 to 2014. The observation site is located on the coast of the Japan Sea in central Japan, where air pollution is actively transported from Asia as well as Japan (Watanabe et al., 2006a, 2011a; Watanabe and Honoki, 2013; Iwamoto et al., 2016). Toyama Prefecture has a steep topography within a horizontal distance of 50 km. The observation site is also located approximately 50 km windward of Mt. Tateyama (altitude, 3015 m) (Fig. 1).

We have made many observations at Mt. Tateyama (Kume et al., 2009; Watanabe et al., 2010, 2011a, 2011b, 2011c, 2012; Watanabe and Honoki, 2013; Uehara et al., 2015). Strong acidic fog or cloud water and high levels of air pollutants have been detected. A serious decline in the forest in the vicinity of Mt. Tateyama has been seen. Especially, serious are the harmful influence of photochemical oxidants, which have increased widely over East Asia, on the vegetation (Kume et al., 2009). Observations of vertical profiles of air pollutants, such as hydroperoxides and O_3, over Imizu City, on the windward side of Mt. Tateyama, are important for evaluating their influence on the ecosystem of a mountainous site in central Japan, where the atmospheric environment is highly affected by extensive air pollution in East Asia.

2.2. Helicopter observation

We used a Robinson R44 helicopter owned by the Advanced Air Corp (http://www.addair.jp/), which is a four-seat light helicopter with a semi-rigid two-bladed main rotor, a two-bladed tail rotor, and a skid landing gear. The cost of chartering this small helicopter is relatively low. Observations were performed in the afternoon (approximately 13 H Japan Standard Time (JST; UTC + 9 H) to 15 H JST) on 23 August 2010, 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014, when the sky was clear or partially cloudy. Two flight observations were made both in the morning (about 10 H JST to 12 H JST) and the afternoon on August 23, 2010. Hydroperoxides in the atmosphere were collected every 2000 ft (approximately 600 m) to an altitude of 10,000 ft (approximately 3000 m) during horizontal circular flights (in a radius of approximately 5 km). The flight speed was approximately 110 km/h. The ranges of the flights were small and are not illustrated in Fig. 1.

A mist chamber made of Pyrex glass (Hatakeyama et al., 1993; Takami et al., 2003) was used to sample of the hydroperoxides. The same type of mist chamber has been used by Takami et al. (2003), Chen et al. (2008) and Chutteang et al. (2012) to sample hydroperoxides. A diluted H_3PO_4 solution (pH = 3.5) added to a small amount of formaldehyde in the mist chamber was nebulized by flowing sample air and dissolved water-soluble gaseous compounds, such as hydroperoxides, into the solution. The mist chamber was placed on the front passenger seat, and the sampling was performed at 4.0 L min^{-1} for 10 min through 6 mm ID Teflon tubing (1 m length). To prevent the photolysis of hydroperoxides during the sampling, the mist chamber was shielded by aluminum foil. Due to the high solubility of hydroperoxides, the trapping yield of H_2O_2 by the mist chamber is approximately 100%. However, the trapping yield of MHP, whose Henry's law constant (M atm^{-1}) is much lower than that of H_2O_2 (Seinfeld and Pandis, 1998), is roughly estimated to be 60%. According to Klippel et al. (2011), the trapping efficiency of MHP into a stripping solution is approximately 60% whereas that of H_2O_2 is 100%. A 50–60% collection efficiency of MHP relative to that of H_2O_2 has been reported (Jackson and Hewitt, 1996; Walker et al., 2006). Therefore, we calculated the trapping efficiency of 60% for MHP and treated the measured MHP concentrations as semi-quantitative values in this paper.

After each hydroperoxide sampling, the helicopter descended at once to a height of approximately 5 m on the campus of Toyama Prefectural University, and the polyethylene bottle that contained the sampling solution was transported to our laboratory. The sample solution was immediately analyzed using an HPLC system (Jasco, LC-2000 Plus) equipped with a separate column (Jasco, Crestpack C18T-5), preceded by a guard column (Jasco Crestpack C18T-5P) that separates H_2O_2 and organic hydroperoxides, such as MHP. The columns were kept at 5 °C. A peroxidase enzyme fluorescence method (Lazrus et al., 1985, 1986) was adopted to detect hydroperoxides with a fluorescence detector (Jasco, FP-2020 Plus). The detailed analytical method is described in Iwama et al. (2011) and Watanabe et al. (2012).

After transporting sample, the helicopter immediately ascended to the higher altitude, and hydroperoxides were collected again. After the next sampling, the helicopter immediately descended near ground level on the campus. The sample was transported to our laboratory and, once again, analyzed at once using our system.

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