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Measurement of hydrogen peroxide and organic hydroperoxide concentrations during autumn in Beijing, China

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ABSTRACT

Gaseous peroxides play important roles in atmospheric chemistry. To understand the pathways of the formation and removal of peroxides, atmospheric peroxide concentrations and their controlling factors were measured from 7:00 to 20:00 in September, October, and November 2013 at a heavily trafficked residential site in Beijing, China, with average concentrations of hydrogen peroxide (H_2O_2) and methyl hydroperoxide (MHP) at 0.55 ppb and 0.063 ppb, respectively. H_2O_2 concentrations were higher in the afternoon and lower in the morning and evening, while MHP concentrations did not exhibit a regular diurnal pattern. Both H_2O_2 and MHP concentrations increased at dusk in most cases. Both peroxides displayed monthly variations with higher concentrations in September. These results suggested that photochemical activity was the main controlling factor on variations of H_2O_2 concentrations during the measurement period. Increasing concentrations of volatile organic compounds emitted by motor vehicles were important contributors to H_2O_2 and MHP enrichment. High levels of H_2O_2 and MHP concentrations which occurred during the measurement period probably resulted from the transport of a polluted air mass with high water vapor content passing over the Bohai Bay, China.

Introduction

Gaseous peroxides, including hydrogen peroxide (H_2O_2) and organic peroxides, such as methyl hydroperoxide and hydroxymethyl hydroperoxide (HMHP), are secondary products generated from photochemical reactions and play important roles in atmospheric chemistry. Peroxides, especially H_2O_2, are important oxidants for the conversion of SO_2 to H_2SO_4 or SO_4^{2-}, which is the main component of $PM_{2.5}$ (particulate matter less than 2.5μm aerodynamic diameter) (Huang et al., 2014; Sun et al., 2015; Zhao et al., 2013; Zhuang et al., 2014). This oxidation reaction occurs mainly in the aqueous phase, such as cloud, rain, fog, and moist surfaces of aerosol, when pH is <4.5 (Hua et al., 2008; Pena et al., 2001; Shen et al., 2012). It has been reported that oxidation of SO_2 in the aqueous phase accounts for 60–80% of the total conversion of SO_2 to sulfate (Calvert et al., 1985).

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Heterogeneous reactions involving H_2O_2 have been suggested as a potential pathway for secondary organic aerosol in fine particles (Claeys et al., 2004; Hua et al., 2008; Liu et al., 2015). Peroxides are also sources and sinks of atmospheric radicals such as OH and HO_2, and are involved in the production of odd-oxygen (*e.g.*, O, O_3) (Reeves and Penkett, 2003). Moreover, H_2O_2/HNO_3 has been suggested as a good indicator for the sensitivity of O_3 production to NO_x (nitrogen oxides) or VOCs (volatile organic compounds) (Chen and Chang, 2006; Peng et al., 2006). The ratios of H_2O_2 to HNO_3 indicating the sensitivity of O_3 production to NO_x or VOCs were different in different areas (Chen and Chang, 2006; Hammer et al., 2002; Peng et al., 2006; Sillman, 1995). He et al. (2010) reported that O_3 production was sensitive to NO_x or VOCs when H_2O_2/HNO_3 was >0.6 or <0.4, respectively, and their results in July 2008 in urban Beijing showed that O_3 production was VOC-sensitive, because the ratios of H_2O_2 to HNO_3 were mostly <0.4. In addition, peroxides may cause declines of crop yields and forest productivity (Chen et al., 2010; Fuhrer and Booker, 2003).

Among peroxides, H_2O_2 is the most abundant in the atmosphere and is generated mainly by the self-reaction of HO_2. HO_2 is mainly from the oxidation of CO or VOCs by OH radicals or O_3, as well as photolysis of formaldehyde.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Another source of H_2O_2 that does not involve HO_2 is the reaction of O_3 and alkenes in the presence of H_2O (Becker et al., 1993; Hatakeyama et al., 1993; Hewitt and Kok, 1991).

$$\text{Alkene} + O_3 \rightarrow \text{Int.}$$

$$\text{Int.} + H_2O \rightarrow H_2O_2$$

Organic peroxides are formed *via* reactions of HO_2 with RO_2 that were mainly produced by the oxidation of alkanes, alkenes and other VOCs (Atkinson, 2000).

$$HO_2 + RO_2 \rightarrow ROOH + O_2$$

Methyl hydroperoxide (MHP) is the most abundant species of organic peroxide in the atmosphere (Hua et al., 2008). In remote areas, MHP is formed *via* the oxidation of CH_4 by OH. However, in polluted areas, the oxidation of VOCs mainly contributes to CH_3O_2, because the oxidation rates of many VOCs for CH_3O_2 radical formation are much faster than that of CH_4.

The main removal pathways of H_2O_2 and organic peroxides in the atmosphere are photolysis, adsorption onto wet surfaces, oxidation by OH, and dry deposition. The rapid reactions of HO_2 or RO_2 with NO can also decrease peroxide concentrations.

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$RO_2 + NO \rightarrow NO_2 + RCHO + HO_2$$

Many studies on atmospheric peroxides have been conducted over the past three decades. Results from field measurements in a forest in central Portugal showed that H_2O_2 concentrations ranged from the detection limit to 0.63 ppb, and MHP concentrations could be as high as 0.1 ppb. Sauer et al. (1994) observed H_2O_2 concentrations ranging from 0.1 to 1.2 ppb in a lighthouse in Brittany, France. Kang et al. (2002) reported that H_2O_2 concentrations in Seoul, South Korea, were high in summer and low in winter, and that H_2O_2 concentrations were positively correlated with temperature and O_3 concentrations. Takami et al. (2003) reported positive correlation between H_2O_2 concentrations and temperature, but negative correlation between H_2O_2 concentrations and relative humidity in their field studies conducted approximately 100 km at the north of Tokyo. They pointed out that polluted air transported from Tokyo caused the increase of H_2O_2 concentrations in the late afternoon at the measurement site. Compared with extensive studies in the United States and Europe, there has been only a limited amount of research on peroxides in Asia, especially China, where SO_2 concentrations are relatively high in many areas (He et al., 2010; Zhang et al., 2010, 2012).

In recent decades, the number of motor vehicles increased dramatically with rapid growth of the economy and progress of urbanization in China. According to the Beijing Statistical Information Net, there were 5.59 million vehicles in Beijing during 2015, compared to 4.81 million in 2010 (http://www.bjstats.gov.cn/tjsj/ndsj/ndsjfpfb/2014n/index_1.html). It is well-known that large quantities of VOCs are emitted from vehicles. The results of a study on VOC sources in Beijing, Shanghai, and Hong Kong showed that vehicle exhausts and gas volatilization are the main sources in Chinese urban air (Cai et al., 2010; Chiang et al., 2007; Geng et al., 2009; Song et al., 2007). Further, Zhang et al. (2009) reported that more than 60% of non-methane hydrocarbons in Beijing are from vehicle exhausts and gas volatilization. The increase of VOCs emissions can generate additional peroxides and O_3 in the city. These oxidants can enhance the oxidizing capacity of the atmosphere, then generate more $PM_{2.5}$, and increase the frequency of haze. These impacts are not only on air quality, the climate and ecosystems, but also on human health in Beijing.

To better understand the formation and removal of gaseous peroxides and their physical and chemical processes in the atmosphere, concentrations of gaseous pollutants and meteorological parameters were measured simultaneously with peroxides during autumn 2013 in Beijing, China.

1. Measurement method

1.1. Measurement site

Gaseous H_2O_2 and organic hydroperoxides were measured in September, October, and November 2013. The sampling site was on the roof of Building #3 of the Chinese Research Academy of Environmental Sciences (40.04°N, 116.42°E), which is in the northeast sector of Beijing, China. There is a heavily trafficked north–south road 500 m to the west, and a small east–west road 100 m to the south. The flow of traffic on these two streets is heavy, especially during the morning rush hour (roughly 7:00 to 9:00) and late afternoon rush hour (roughly 17:00 to 20:00). There are large residential areas east and north of the monitoring site.

1.2. Sampling method

A mist chamber filled with 6 mL of pH-7 deionized-distilled water (Fig. 1) was used to take air samples at hourly intervals from 7:00 to 19:00 every day. A total of 125 samples were obtained. Samples were collected at a flow rate of 2.5 L/min

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