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

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ARTICLE INFO

Article history:
Received 22 April 2016
Revised 7 September 2016
Accepted 5 December 2016
Available online 7 January 2017

Keywords:
Peroxide
Formation
Controlling factor
Volatile organic compound
Transport of polluted air mass

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 (H₂O₂) and methyl hydroperoxide (MHP) at 0.55 ppb and 0.063 ppb, respectively. H₂O₂ concentrations were higher in the afternoon and lower in the morning and evening, while MHP concentrations did not exhibit a regular diurnal pattern. Both H₂O₂ 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 H₂O₂ concentrations during the measurement period. Increasing concentrations of volatile organic compounds emitted by motor vehicles were important contributors to H₂O₂ and MHP enrichment. High levels of H₂O₂ 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.

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Heterogeneous reactions involving H$_2$O$_2$ 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$_2$O$_2$/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; Hammer et al., 2002; Peng et al., 2006). The ratios of H$_2$O$_2$ 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$_2$O$_2$/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$_2$O$_2$ 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$_2$O$_2$ 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 photoysis of formaldehyde.

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

Another source of H$_2$O$_2$ that does not involve HO$_2$ is the reaction of O$_3$ and alkenes in the presence of H$_2$O (Becker et al., 1993; Hatakeyama et al., 1993; Hewitt and Kok, 1991).

\[ \text{alkene} + \text{O}_3 \rightarrow \text{Int.} \]

\[ \text{Int.} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \]

Organic peroxides are formed via reactions of H$_2$O$_2$ with RO$_2$ that were mainly produced by the oxidation of alkanes, alkenes and other VOCs (Atkinson, 2000).

\[ \text{HO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{O}_2 \]

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$_3$O$_2$, because the oxidation rates of many VOCs for CH$_3$O$_2$ radical formation are much faster than that of CH$_4$.

The main removal pathways of H$_2$O$_2$ 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.

\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \]

\[ \text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{RCHO} + \text{HO}_2 \]

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$_2$O$_2$ 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$_2$O$_2$ concentrations ranging from 0.1 to 1.2 ppb in a lighthouse in Brittany, France. Kang et al. (2002) reported that H$_2$O$_2$ concentrations in Seoul, South Korea, were high in summer and low in winter, and that H$_2$O$_2$ concentrations were positively correlated with temperature and O$_3$ concentrations. Takami et al. (2003) reported positive correlation between H$_2$O$_2$ concentrations and temperature, but negative correlation between H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ 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 northeastern 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...
for 1 hr. Sampling efficiency was studied using two mist chambers connected in series to collect and analyze gaseous H$_2$O$_2$ at 3–4 ppb and MHP at 0.6–0.7 ppb. The results showed that the sampling efficiency was 98.6% for H$_2$O$_2$ and 73% for MHP. MHP concentrations obtained during the measurement period were corrected for its low sampling efficiency.

### 1.3. Analysis method

After sampling, peroxides were immediately analyzed using a high-performance liquid chromatography (HPLC) system equipped with a fluorescence detector (Shimadzu, LC-20A, Tokyo, Japan) (Chen et al., 2008). They were first separated with an octadecylsilyl-II (ODS-II) column (GL, Science; 5 μm, 4.6 × 250 mm$^2$, Tokyo, Japan), and then reacted with p-hydroxyphenylacetic acid (POPHA) in the presence of horseradish peroxidase (HRP) at the optimum pH of fluorescence reaction (>6.0), to generate a fluorescent dimer quantitatively. Then pH of the reacted solution was adjusted to >10, the optimum for fluorescence detection, by adding alkaline solution before detection. Peroxide concentrations were determined by measuring fluorescence of the dimer, using a fluorescence detector with the excitation and emission wavelengths of 315 and 405 nm, respectively. The flow rates of mobile phase (0.3 mmol/L H$_3$PO$_4$, pH = 3.5), reaction reagent (5 activity units/mL HRP, 0.1 mmol/L POPHA, 0.01 mol/KH$_2$PO$_4$), and alkaline solution (0.8 M NH$_4$Cl/NH$_3$·H$_2$O) were 0.5, 0.2, and 0.1 mL/min, respectively. The sample amount into HPLC was 20 μL.

Calibration curves for H$_2$O$_2$ and MHP were generated daily with H$_2$O$_2$ and MHP standard solutions. A standard solution of H$_2$O$_2$ was used to calibrate hydroxymethyl hydroperoxide (HMHP), because HMHP decomposed to H$_2$O$_2$ after pH of the solution containing the fluorescent substance was adjusted to 10.5. Detection limits were equated to 20 times the standard deviation of a blank; they were 1 part per trillion (ppt) for H$_2$O$_2$ and HMHP and 10 ppt for MHP. To maintain enzyme activity and prevent peroxide decomposition, the horseradish peroxidase and ODS-II column were stored in a column oven at temperature of 4°C. All connecting pipes and connectors in the system were made of Teflon to reduce peroxide adsorption or decomposition on the metal surfaces.

Concentrations of other trace gases, such as O$_3$ and SO$_2$, and meteorological factors, such as temperature and relative humidity, were measured simultaneously at the site.

### 2. Results and discussion

#### 2.1. Peroxide concentrations

Sampling was conducted mainly on sunny days, but some measurements were made on partly cloudy days. Light rain was recorded only on September 23. During the measurement periods, the weather was dry and all relative humidity values were <60%, except for one sample. Solar radiation and temperature decreased from September through November. Wind speeds were <1.0 m/sec on most days. The average concentrations of O$_3$, SO$_2$, and NO$_x$ measured in September, October, and November 2013 are summarized in Table 1. O$_3$ concentrations were in the range of 5.0–81.3 ppb. The maximum concentration of O$_3$ was observed at 16:00 on 21 September 2013, when the concentrations of SO$_2$ (0.9 ppb) and NO$_x$ (21.1 ppb) were low. SO$_2$ concentrations were <5.0 ppb on most days and did not exhibit a clear diurnal pattern. NO$_x$ concentrations were generally in the range of 0.7–67.4 ppb and were higher in the morning before 11:00, after which they decreased through 16:00. Concentrations of O$_3$ were higher in September than in October and November, whereas SO$_2$ and NO$_x$ concentrations were higher in October and November than in September.

During the measurement period, H$_2$O$_2$ and MHP were detected quantitatively. HMHP was occasionally detected. The low HMHP concentrations can be attributed to the heterogeneous decomposition of HMHP on the glass surface during sampling and its low concentration in the atmosphere (Neeb et al., 1997; Sauer et al., 2001). H$_2$O$_2$ and MHP concentrations measured in September, October, and November 2013 are summarized in Table 2 and Fig. 2. Concentrations of H$_2$O$_2$ and MHP were 0.10–2.4 ppb and 0.0040–0.27 ppb, with means of 0.55 ppb and 0.063 ppb, respectively. The maximum concentrations of H$_2$O$_2$ and MHP were recorded at 16:00 and 18:00, respectively, on September 21. The average H$_2$O$_2$ concentration was 7 times the average MHP concentration, the indication being that H$_2$O$_2$ was the dominant gaseous peroxide in the atmosphere during the measurement period.

Table 3 shows the measurement results of gaseous peroxides in different observation sites. H$_2$O$_2$ concentrations in this measurement were similar to those measured during...
July 2006 in Guangzhou (Hua et al., 2008) and July 2008 in Beijing (He et al., 2010), whereas MHP concentrations were lower than those measured in Beijing and Guangzhou during summer 2006 (Hua et al., 2008; Zhang et al., 2012). H$_2$O$_2$ concentrations measured in the present study were obviously higher than those reported in various cities of other countries. The average H$_2$O$_2$ concentration in Seoul, South Korea, was only 0.059 ppb in October, when solar radiation and temperature are the highest (Kang et al., 2002). The average concentration of H$_2$O$_2$ at WISTA Scientific Park in Berlin, Germany was <0.25 ppb in May, when H$_2$O$_2$ concentrations are higher than any other time of the year (Möller, 2009). The concentrations of MHP we measured were most consistent with those measured in Berlin, Germany (Moortgat et al., 2002), but lower than those measured in a forested area of Portugal, where the maximum concentration was 0.64 ppb (Sauer et al., 2001).

2.2. Variation in peroxide concentrations

Fig. 3 depicts the diurnal variations of peroxide concentrations and their controlling factors during the monitoring period. O$_3$ concentrations showed a diurnal pattern similar to that of solar radiation, with high concentrations around noon and low values in the morning and late afternoon. The maximum concentration of O$_3$ was always observed at 14:00–15:00 (Fig. 3c). H$_2$O$_2$ and MHP varied remarkably during the course of each day and the variation of H$_2$O$_2$ concentration was not the same at the same time every day, revealing the complicity of their formation and destruction in the atmosphere. It was shown that for all days H$_2$O$_2$ concentrations increased from sunrise, reached maxima value during 13:00 and 16:00, and then decreased after generally summarizing the variation trend of hydrogen peroxide in a day (Fig. 3c). This is because higher solar radiation and temperatures during the daytime can accelerate photochemical reactions and cause more formation of O$_3$ and H$_2$O$_2$. Similar results of diurnal variations of H$_2$O$_2$ concentrations have been reported in previous studies (He et al., 2010; Hua et al., 2008; Sauer et al., 2001; Watanabe and Tanaka, 1995).

MHP concentrations did not exhibit a clear diurnal pattern (Fig. 3c). This was different from the pattern reported in previous studies. Jackson and Hewitt (1996) reported that MHP concentrations measured in a forest in Portugal were higher during the day than during the night. Zhang et al. (2012) observed that MHP concentration was lower than during the night. It is noteworthy that in most cases, both H$_2$O$_2$ and MHP concentrations increased again around 18:00, when solar radiation had clearly decreased (Fig. 3c). The maximum concentrations of MHP occurred after 18:00 in a third of cases. Generally, photochemical reactivity gradually weakened and the rate of formation of photochemical products decreased with the decreasing solar radiation. Relative humidity increases at sunset in addition to boundary layer descent, resulting in an increase of the physical deposition of peroxides (Das and Hussain, 1999). Consequently, the concentrations of H$_2$O$_2$ and MHP decrease. Watkins et al. (1995) observed a rapid decline of H$_2$O$_2$ concentrations after 18:00 at Niwot Ridge, Colorado, USA, which was attributed mainly to surface deposition under a nocturnal inversion layer. However, in the present study, the concentrations of H$_2$O$_2$ and MHP increased again in the late afternoon. This result implies that more H$_2$O$_2$ and MHP were generated in the late afternoon, and that their amounts were sufficient to offset their deposition loss. The formation of H$_2$O$_2$ and MHP may result from the ozonolysis of alkenes (Paulson and Orlando, 1996). In our study, the sampling site was close to two roads with heavy traffic flow, and the number of motor vehicles was larger at dusk than in the daytime. This may have increased the amount of hydrocarbons emitted at dusk. Results from August 2013 showed that the average concentrations of total alkanes, total alkenes, and total aromatics between 17:00 and 20:00 were 1.8, 2.1, and 2.5 times those observed in the daytime (10:00–16:00), respectively (data unpublished). Therefore, the reactions of VOCs with O$_3$ or NO$_3$ radicals generated additional RO$_2$ and HO$_2$ radicals, which may have been the reason for the increase of H$_2$O$_2$ and MHP concentrations at dusk (Kleinman et al., 2005; Lee et al., 2000; Salisbury et al., 2001). It is also reported that a second MHP concentration peak sometimes occurred in the late afternoon in Beijing, which can be attributed to pollutant emissions during heavy traffic hours (Zhang et al., 2012). Further studies are needed to clarify this potential source of peroxides in the late afternoon.

As shown in Table 2, the concentrations of H$_2$O$_2$ and MHP were higher in September than October and November. This was caused by an increase of peroxide generation in September, when both light intensity and temperature were higher than in October and November.

### 2.3. Correlations between peroxides and their controlling factors

The formation of atmospheric H$_2$O$_2$ and MHP is affected by chemical pollutants such as O$_3$, NO$_x$, and VOCs. Moreover,

### Table 1 – Concentrations of O$_3$, SO$_2$, and NO$_x$ measured in September, October, and November 2013.

<table>
<thead>
<tr>
<th>Month</th>
<th>Average concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_3$</td>
</tr>
<tr>
<td>September</td>
<td>24.7 ± 20.4</td>
</tr>
<tr>
<td>October</td>
<td>17.3 ± 9.6</td>
</tr>
<tr>
<td>November</td>
<td>17.9 ± 8.9</td>
</tr>
</tbody>
</table>

NO$_x$: nitrogen oxides.

### Table 2 – Summary of H$_2$O$_2$ and MHP concentrations observed in 2013.

<table>
<thead>
<tr>
<th>Peroxides</th>
<th>Months</th>
<th>Concentration (ppb)</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>September</td>
<td>0.10</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>October</td>
<td>0.16</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>November</td>
<td>0.14</td>
<td>0.38</td>
</tr>
<tr>
<td>MHP</td>
<td>September</td>
<td>0.0040</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>October</td>
<td>0.0060</td>
<td>0.051</td>
</tr>
<tr>
<td></td>
<td>November</td>
<td>0.017</td>
<td>0.040</td>
</tr>
</tbody>
</table>

MHP: methyl hydroperoxide.
meteorological parameters, including solar radiation intensity, relative humidity, and temperature, are important determinants of the concentrations of H$_2$O$_2$ and MHP. We analyzed correlations between H$_2$O$_2$ concentrations and other factors to elucidate which factors affect H$_2$O$_2$ concentrations (Fig. 4, Table 4). We found strong positive correlation between concentrations of H$_2$O$_2$ and O$_3$ (Fig. 4a). Similar results have been reported in earlier studies (Jackson and Hewitt, 1996; Kang et al., 2002; Ren et al., 2009; Takami et al., 2003). This positive correlation reflects the fact that both H$_2$O$_2$ and O$_3$ are photochemical products. O$_3$ plays an important role in generating H$_2$O$_2$ because the photolysis of O$_3$ in the presence of water vapor generates OH radicals, and the reactions of hydrocarbons with O$_3$ or OH radicals can produce the HO$_2$ radical, a precursor of H$_2$O$_2$.

Regarding NO$_x$, Lee et al. (2000) and Sauer et al. (2001) reported that high NO$_x$ concentrations inhibit the formation of H$_2$O$_2$ by scavenging peroxy radicals such as HO$_2$ and RO$_2$. In the present study, correlations between H$_2$O$_2$ and NO$_x$ varied during the measurement period. H$_2$O$_2$ concentrations were unaffected by NO$_x$ when NO$_x$ concentrations were <35 ppb. In contrast, H$_2$O$_2$ concentrations decreased sharply when NO$_x$ concentrations exceeded 35 ppb. NO is expected to suppress H$_2$O$_2$ formation because the rate coefficient of the reaction between HO$_2$ and NO is nearly twice that of the bimolecular combination of HO$_2$ (Sander et al., 2003). Similar observations have been reported in other studies (He et al., 2010; Sauer et al., 2001; Walker et al., 2006).

As shown in Table 4, H$_2$O$_2$ concentrations were positively correlated with temperature, which is in agreement with other studies (Chen et al., 2008; Jackson and Hewitt, 1996; Takami et al., 2003). High temperatures can accelerate photochemical reactions, thereby promoting H$_2$O$_2$ generation. Higher temperatures are also associated with higher absolute humidity, and increasing water vapor concentrations facilitate generation of HO$_2$.

Increases in SO$_2$ concentrations can reduce H$_2$O$_2$ concentration when the relative humidity is sufficiently high, because H$_2$O$_2$ can react quickly with SO$_2$ to generate H$_2$SO$_4$ or SO$_4^{2-}$ in the liquid phase (pH < 4.5). In our study, there was only weak negative correlation between SO$_2$ and H$_2$O$_2$, with a small correlation coefficient ($r = 0.06$). We have reported that H$_2$O$_2$ concentrations in Nagano, Japan decrease sharply when the SO$_2$ concentration is >2.5 ppb (Chen et al., 2008). This result was obtained when the relative humidity was >60% in most cases. In contrast, the relative humidity was almost always <60% in the present study. It is therefore concluded that relative humidity <60% is insufficient to eliminate H$_2$O$_2$ via the aqueous phase reactions of SO$_2$ with H$_2$O$_2$.

Several studies have indicated that H$_2$O$_2$ concentrations decrease with increasing relative humidity, because H$_2$O$_2$ is

![Fig. 2 – Concentrations of H$_2$O$_2$ and MHP measured in September, October, and November 2013. MHP: methyl hydroperoxide.](image)

### Table 3 – Measurements of gaseous H$_2$O$_2$ and MHP in different observation sites.

<table>
<thead>
<tr>
<th>Observation site</th>
<th>Measurement period</th>
<th>Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, China</td>
<td>12 July–30 September, 2008</td>
<td>H$_2$O$_2$, d.l.–2.34 ppb; MHP, d.l.–0.95 ppb</td>
<td>He et al. (2010)</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Summer of 2006, 2007, and 2008</td>
<td>MHP, 0.01–1.10 ppb</td>
<td>Zhang et al. (2012)</td>
</tr>
<tr>
<td>Rural site, Guangzhou, China</td>
<td>July 2006</td>
<td>H$_2$O$_2$, -20 ppt–4.6 ppb</td>
<td>Hua et al. (2008)</td>
</tr>
<tr>
<td>Hong Kong, China</td>
<td>Four seasons during 2011–2012</td>
<td>MHP, -35 ppt–0.8 ppb</td>
<td>Guo et al. (2014)</td>
</tr>
<tr>
<td>Mount Tai, China</td>
<td>March 22–April 24, June 16–July 20, 2007</td>
<td>Peroxides, spring, 0.17 ± 0.16 ppb (max 1.28 ppb); summer, 0.55 ± 0.67 ppb (max 3.55 ppb)</td>
<td>Ren et al. (2009)</td>
</tr>
<tr>
<td>Oku-Nikko, Japan</td>
<td>July to August in 1998, 1999 and 2000</td>
<td>H$_2$O$_2$, 0.2–1.6 ppb</td>
<td>Takami et al. (2003)</td>
</tr>
<tr>
<td>Red pine forest, Nagano, Japan</td>
<td>Several periods in 2000–2002</td>
<td>H$_2$O$_2$, autumn, 0.10 ± 0.126 ppb</td>
<td>Chen et al. (2008)</td>
</tr>
<tr>
<td>Seoul, Korea</td>
<td>January 2002–April 2004</td>
<td>H$_2$O$_2$, autumn, 0.07–0.87 ppb</td>
<td>Lee et al. (2008)</td>
</tr>
<tr>
<td>Forested area, Portugal</td>
<td>June-July 1994</td>
<td>H$_2$O$_2$, -15 ppt–1.38 ppb</td>
<td>Sauer et al. (2001)</td>
</tr>
<tr>
<td>Berlin, Germany</td>
<td>July–August 1998</td>
<td>MHP, -15 ppt–0.64 ppb</td>
<td>Moortgat et al. (2002)</td>
</tr>
<tr>
<td>WISTA Scientific Park, Berlin, Germany</td>
<td>May, 2000–July, 2001</td>
<td>H$_2$O$_2$, September, 0.06 ± 0.04 ppb</td>
<td>Möller (2009)</td>
</tr>
<tr>
<td>Jungfraujoch, Switzerland</td>
<td>February–March 2003</td>
<td>MHP, 0.051 ± 0.055 ppb (max 0.38 ppb)</td>
<td>Walker et al. (2006)</td>
</tr>
</tbody>
</table>

MHP: methyl hydroperoxide.

* Range: values for the lower 10% and upper 90%.
highly soluble in water (Das and Husain, 1999; Takami et al., 2003; Yamada et al., 2002). Nevertheless, no clear, negative correlation between H$_2$O$_2$ concentrations and relative humidity was apparent in our results, owing to the lower relative humidity during the study period. This finding is consistent with Hasson and Paulson (2003) and Ren et al. (2009), who noted that weak negative correlation between H$_2$O$_2$ concentrations and relative humidity may be observed only when relative humidity exceeds 60%. It has also been indicated that gas-phase H$_2$O$_2$ is removed from the gas-phase by aqueous aerosols only when relative humidity is at

Fig. 3 – Diurnal variation of peroxide concentrations and their controlling factors during monitoring period.

Fig. 4 – Interrelation of H$_2$O$_2$ and O$_3$ (a), MHP and O$_3$ (b). MHP: methyl hydroperoxide.
least 60% (Das and Husain, 1999). Dissolution on the wet surface of aerosols is an important pathway for the removal of H$_2$O$_2$. The total amount of liquid water in aerosols governs the removal rate of H$_2$O$_2$. In other words, there is negative correlation between aerosol liquid water content and gas-phase H$_2$O$_2$ concentrations. It is noteworthy that inorganic salts, particularly ammonium sulfate, are major components of ambient aerosols in Beijing (Huang et al., 2014; Zhao et al., 2013; Zhuang et al., 2014). The deliquescence points of most inorganic salts occur at relative humidity $>$60%. At low relative humidity, most aerosols containing a large fraction of inorganic salts are usually in dry form. When relative humidity is between 30% and 60%, one would not expect a corresponding variation in gas-phase H$_2$O$_2$ concentrations. In the correlation between H$_2$O$_2$ and dew point, the data were clearly divided into two groups, the first with relatively high H$_2$O$_2$ concentrations and dew points $>$ 8°C, and the second with relatively low H$_2$O$_2$ concentrations and dew points $<$ 5°C. This dichotomy is specifically discussed in Section 2.4.

Solar radiation is a driving force for photochemical reactions. Although positive correlation between solar radiation and H$_2$O$_2$ concentrations was therefore expected, we did not observe any clear correlation in our study. Factors other than solar radiation must also affect H$_2$O$_2$ concentrations especially at sunset. These factors may include the reaction of hydrocarbons with, inter alia, OH and O$_3$ (Section 2.2) and regional transport (Section 2.4). There was no clear correlation between H$_2$O$_2$ and wind speed when that speed was $<$ 1 m/sec, but there was negative correlation when the speed exceeded 1 m/sec, because stronger wind can reduce pollutant concentrations.

MHP concentrations were positively correlated with O$_3$ (Fig. 4b) and temperature (Table 4), but showed no correlation with other environmental factors.

### 2.4. Case study

There was a great difference in H$_2$O$_2$ levels during the measurement periods in September. The weather was sunny except for September 23, and solar radiation was weaker on September 21 than September 24 and 25, whereas H$_2$O$_2$ concentrations were much higher on September 21 (Fig. 2, Table 5). It is known that there are abundant precursors (VOCs) of peroxides, and VOCs are mainly from motor vehicle emissions in Beijing (Song et al., 2007; Zhang et al., 2009). It was the third day of Mid-Autumn holiday on September 21, and it was weekdays on September 24 and 25. From the statistics of the traffic flow in highway in recent years, it is reported that there were many people leaving from Beijing to have a trip or go back to hometown during 3-day holiday, such as Mid-Autumn Festival. Usually, traffic returning to Beijing started from 14:00 or 15:00, and reached a peak at 17:00 or 18:00 on the third day. In contrast, H$_2$O$_2$ concentrations increased obviously from 14:00, reached the maximum value at 16:00 and then decreased significantly on September 21. The variation of H$_2$O$_2$ concentrations was different from the traffic data on September 21. Therefore, it can be conjectured that high levels of H$_2$O$_2$ on September 21 were not caused by the oxidation of VOCs.

As for other environmental factors, SO$_2$ concentrations were lower on September 21 than September 24 and 25. The NO$_x$ concentration was lower on September 21 than September 25, but higher than September 24. It appears that SO$_2$ and NO$_x$ were not primarily responsible for the lower H$_2$O$_2$ concentration on September 24 and 25. Atmospheric pressure was lower, and the temperature, relative humidity, and dew point were higher on September 21 than September 24 and 25. A high dew point indicates high absolute humidity, or a large percentage of water vapor in the atmosphere. This implies that different air masses were sampled on September 21 relative to September 24 and 25. To investigate the above implication, we studied backward trajectories and wind field on September 21, 24, and 25 (Figs. 5 and 6). It is apparent from these figures that the air mass near the ground surface on September 21 originated from Liaoning Province. It then passed over Bohai Bay, through Hebei Province and Tianjin, finally reached the sampling site. In contrast, the air mass on September 24–25 came from high altitudes above Mongolia and Inner Mongolia and quickly descended to lower altitudes near Beijing. Compared with Mongolia and Inner Mongolia, more VOCs and NO$_x$
were emitted into the atmosphere over Liaoning, Hebei, and Tianjin. These pollutants increased O3 via chemical reactions, thereby increasing H2O2 during transportation period or after polluted air mass transported to the sampling site through chemical reactions on September 21.

Furthermore, photochemical reactions producing secondary oxidants could have become more active when the air mass from Liaoning traversed Bohai Bay, owing to stronger solar radiation over the bay. In summary, the transport of a polluted air mass might explain why the concentrations of H2O2 and O3 were higher on September 21 than September 24 and 25 at the sampling site. In addition, high water vapor content on September 21 could have augmented the formation of H2O2 (Tremmel et al., 1993), because H2O can react with O(1D) formed by O3 photolysis to produce HO2 radicals and consequently increase H2O2.

3. Conclusions

Atmospheric concentrations of H2O2 and MHP and their controlling factors were measured at a heavily trafficked residential site in Beijing, in September, October, and November 2013. During the measurement period, average concentrations of H2O2 and O3 were 0.55 and 0.063 ppb, with maximum values of 2.4 and 0.27 ppb, respectively. In most cases, H2O2 concentrations were higher in the afternoon than in the morning and evening. In contrast, we found there was no clear diurnal variation of MHP concentrations. The concentrations of both peroxides increased again after sunset in most cases. H2O2 and MHP concentrations were higher in September than October and November, they were positively correlated with O3 concentrations and temperature, but negatively correlated with NO concentrations. Based on these findings, we concluded that H2O2 was generated mainly by photochemical reactions during the measurement period. Increasing hydrocarbon amounts emitted by motor vehicles were important contributors to H2O2 and MHP enrichment. In addition, a polluted air mass with high water vapor content that was transported from urban areas and passed over the Bohai Bay increased H2O2 concentrations during the measurement period.

Acknowledgments

This work was supported by the International Cooperation Project of MOST (No. 2012DFG90290), the National Natural Science Foundation of China (No. 4225001046), National Department Public Benefit Research Foundation (No. 201509014), and the Basic Foundation for Public Benefit-Research Academies from Centre Government (No. 2010KYYW02). We thank the participants in our measurements for their help and support throughout this research.
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