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Atmospheric hydrogen peroxide and organic hydroperoxides during PRIDE-PRD'06, China: their concentration, formation mechanism and contribution to secondary aerosols

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Abstract

Atmospheric hydrogen peroxide (H_2O_2) and organic hydroperoxides were measured from 18 to 30 July in 2006 during the PRIDE-PRD'06 campaign at Backgarden, a rural site located 48 km north of Guangzhou, a mega-city in southern China. A ground-based instrument was used as a scrubbing coil collector to sample ambient air, followed by on-site analysis by high-performance liquid chromatography (HPLC) coupled with post-column derivatization and fluorescence detection. The H_2O_2 mixing ratio over the 13 days ranged from below the detection limit to a maximum of 4.6 ppbv, with a mean (and standard deviation) of (1.26±1.24) ppbv during the daytime (08:00–20:00 LT). Methyl hydroperoxide (MHP), with a maximum of 0.8 ppbv and a mean (and standard deviation) of (0.28±0.10) ppbv during the daytime, was the dominant organic hydroperoxide. Other organic peroxides, including bis-hydroxymethyl hydroperoxide (BHMP), peroxyacetic acid (PAA), hydroxymethyl hydroperoxide (HMHP), 1-hydroxy-ethyl hydroperoxide (1-HEHP) and ethyl hydroperoxide (EHP), were detected occasionally. The concentration of H_2O_2 exhibited a pronounced diurnal variation on sunny days, with a peak mixing ratio in the afternoon (12:00–18:00 LT), but lacked an explicit diurnal cycle on cloudy days. Sometimes a second peak mixing ratio of H_2O_2 was observed during the evening, suggesting that H_2O_2 was produced by the ozonolysis of alkenes. The diurnal variation profile of MHP was, in general, consistent with that of H_2O_2. The estimation indicated that in the morning the H_2O_2 detected was formed mostly through local photochemical activity, with the rest probably attributable to vertical transport. It is notable that relatively high levels of H_2O_2 and MHP were found in polluted air. The unexpectedly high level of HO_2 radicals detected in this region can account for the production of hydroperoxides, while the high level of NO_x suppressed the formation of hydroperoxides significantly. High concentrations of hydroperoxides were detected in samples of rainwater collected in a heavy shower on 25 July when a typhoon passed through, indicating that a considerable mixing ratio of hydroperoxides, particularly MHP, resided above the upper boundary layer, which might be transported

on a regional scale and further influence the redistribution of HO_x and RO_x radicals. It was found that hydroperoxides, in particular H_2O_2, play an important role in the formation of secondary sulfate in the aerosol phase, where the heterogeneous reaction might contribute substantially. A negative correlation between hydroperoxides and water-soluble organic compounds (WSOC), a considerable fraction of the secondary organic aerosol (SOA), was observed, providing field evidence for the importance of hydroperoxides in the formation of SOA found in previous laboratory studies. We suggest that hydroperoxides act as an important link between sulfate and organic aerosols, which needs further study and should be considered in current atmospheric models.

1 Introduction

A series of hydroperoxides, including hydrogen peroxide (H_2O_2) and organic hydroperoxides (ROOH), such as methylhydroperoxide (MHP, CH_3OOH), hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$), 1-hydroxy-ethyl hydroperoxide (1-HEHP, $CH_3CH(OH)OOH$), peroxyacetic acid (PAA, $CH_3C(O)OOH$) and ethylhydroperoxide (EHP, CH_3CH_2OOH), have been measured in the atmosphere since the measurement of organic hydroperoxides was pioneered in the 1980s by Hellpointner and Gäb (1989). These reactive species play significant roles in atmospheric processes, such as acid precipitation, cycling of HO_x radicals, and formation of secondary organic aerosol (SOA). H_2O_2 is considered to be the most important oxidant for the conversion of S (IV) to sulfuric acid and secondary sulfate in cloud, fog and rain water at pH<5, thus contributing significantly to the acidification of clouds and rain (Penkett et al., 1979; Calvert et al., 1985; Fung et al., 1991; Pena et al., 2001). Organic peroxides such as MHP, HMHP, and PAA are able to oxidize SO_2, but only when H_2O_2 is limited (Lind et al., 1987; Zhou and Lee, 1992). For instance, HMHP is much more soluble than H_2O_2 ($H_{H_2O_2}=7.7\times10^4\,M\,atm^{-1}$ and $H_{HMHP}=1.7\times10^6\,M\,atm^{-1}$ at 298 K, Sander et al., 2003) and can decompose rapidly into H_2O_2 and HCHO in the aqueous phase when pH>5.0 (O'Sullivan et al., 1996; Chen et al., 2008). In addition, H_2O_2 and MHP can serve as temporary reservoirs of odd-hydrogen radicals (OH, HO_2, CH_3O_2) in the troposphere, because their photolysis and other reactions will lead to the regeneration of OH radicals, and are intimately involved in the production of odd-oxygen (e.g. O, O_3) (Madronich and Calvert, 1990; Lightfoot et al., 1992; Reeves and Penkett, 2003). For example, MHP, which is the most abundant organic hydroperoxide in the atmosphere, and has an atmospheric lifetime of 2–3 days and a low level of solubility in water (Cohan et al., 1999; Wang and Chen, 2006), can be transported to the upper troposphere at a regional scale without scavenging under deep convection conditions. As a result, this transportation probably leads to the redistribution of OH radicals in different regions and different altitudes (Jaeglé et al., 1997; Wennberg et al., 1998; Cohan et al., 1999; Mari et al., 2000; Ravetta et al., 2001), and H_2O_2 and organic hydroperoxides can be used as indicators of the oxidizing capacity of the troposphere (Thompson, 1992). Tropospheric aerosols play an important role in the Earth's atmosphere and in the climate system. Aerosols scatter and absorb solar radiation (direct effect) (Andreae and Crutzen, 1997), change cloud characteristics in many ways (indirect effect) (e.g. Navakov and Penner, 1993; Lohmann and Feichter, 2005), and facilitate heterogeneous and multiphase chemistry (Ravishankara, 1997). Increasing attention is being paid to the organic matter that represents a substantial fraction of tropospheric aerosols (Andreae and Crutzen, 1997). Recently, several laboratory studies have revealed that secondary organic aerosol (SOA) can be formed from isoprene and its gas-phase oxidation products through acid-catalyzed aqueous-phase oxidation with hydrogen peroxide, a remarkably close analogy with atmospheric secondary sulfate formation (Claeys et al., 2004; Böge et al., 2006; Kroll et al., 2006).

No significant direct emission of H_2O_2 or organic hydroperoxides from natural or anthropogenic sources has been found, and it is believed that the majority of the H_2O_2 and ROOH in the gas phase are formed via the bimolecular and termolecular recombination of peroxy (HO_2 and RO_2) radicals during the daytime. The only known mechanism for the formation of peroxides in the absence of light is the ozonolysis reaction of alkenes (Gäb et al., 1985; Becker et al., 1990, 1993; Valverde-Canossa et

al., 2004), which is discussed in detail in Sect. 3.4. This reaction is the main source of the 1-hydroxyalkylhydroperoxides (1-HAHP) and a source of OH radicals (Atkinson and Aschmann, 1993; Paulson and Orlando, 1996).

Formation of HO_2 radicals is predominantly through the photo-oxidation of carbon monoxide (CO) and volatile organic compounds (VOC) by the OH radical (described in detail by Lightfoot et al., 1992). The second significant part of HO_2 is formed during the degradation of HCHO and other aldehydes by photolysis or by reaction with OH radicals (Buffalini et al., 1972; Su et al., 1979). Furthermore, the ozonolysis of alkenes, the decomposition of peroxy acetyl nitrate (PAN), and the photodegradation of aromatic hydrocarbons will provide a source of HO_2 (Finlayson-Pitts and Pitts, 1986; Seuwen and Warneck, 1995). Alkylperoxy radicals (RO_2) are produced by the reaction of OH radicals with alkanes, e.g. CH_4, in the presence of oxygen, and by the decomposition of alkyl-substituted, excited Criegee biradicals (Atkinson, 1994; Hatakeyama and Akimoto, 1994; Gäb et al., 1995).

The sinks for gaseous H_2O_2 and organic peroxides can be classified according to different processes, including washout through fog droplets and adsorption on water-covered aerosols or other wet surfaces; dry deposition; photolysis; and reaction with OH radicals. Although the importance of the individual processes might differ with regard to the water solubility of the organic peroxides (Gunz and Hoffmann, 1990; Watkins et al., 1995a, b), the washout and adsorption processes on wet surfaces are expected to be dominant.

Field, laboratory and modeling studies have all indicated that the generation and behavior of gas-phase H_2O_2 and organic ROOHs are affected by the levels of chemical components such as NO_x, CO, CH_4, and VOC. Additionally, meteorological parameters, including solar radiation, relative humidity, temperature, and pressure are of great importance in controlling the production and the loss of hydroperoxides (Lee et al., 2000).

Over the past two decades, the distribution and roles of H_2O_2 and CH_3OOH in the atmosphere have been investigated by various methods on land, onboard ship, and aboard aircraft (Hellpointner and Gäb, 1989; Hewitt and Kok, 1991; Das and Aneja, 1994; Fels and Junkermann, 1994; Watkins et al., 1995a, 1995b; Staffelbach et al., 1996; Heikes et al., 1996; Jackson and Hewitt, 1996; Sauer et al., 1997, 2001; Lee et al., 1993, 1995, 1998, 2000, 2008; Morgan and Jackson, 2002; Grossmann et al., 2003; François et al., 2005; Walker et al., 2006; Kim et al., 2007). The mixing ratios of H_2O_2 typically lie between 0.5 ppbv and 5 ppbv worldwide. The MHP mixing ratios measured in earlier studies are between several pptv and 2.7 ppbv (O'Sullivan et al., 1999; Lee et al., 2000). Lee et al. (1998) reported a maximum of 14 ppbv H_2O_2 and attributed this high value to a new mechanism of formation – direct production with biomass burning plumes, as well as secondary photochemical production. O'Sullivan et al. (1999) observed maximum H_2O_2 and MHP mixing ratios of 11.5 ppbv and 2.7 ppbv, respectively, during flights in the marine troposphere and attributed these high values to the strong Asian outflow. Moreover, the concentrations of H_2O_2 determined in rainfall samples ranged from 0.1 μMol/L to 300 μMol/L (Hellpointner and Gäb, 1989; Jacob et al., 1990; Hewitt and Kok, 1991; Sauer et al., 1996, 1997; Pena et al., 2001; Morgan and Jackson, 2002). Although numerous field measurements of H_2O_2 and organic peroxides have been made, most of them were done at 25°–55° N, including North America, Brazil, Europe, Greenland, South Africa, and in the Atlantic and the northwestern and central tropical Pacific (Lee et al., 2000). To our knowledge, data for hydroperoxides on land are not available for the East Asia low latitude region, where the atmospheric chemistry may be significantly distinguished from other regions on earth. Accompanying rapid industrialization, East Asia has increasing amounts of O_3 precursor trace gases (carbon monoxide, nitrogen oxides, and hydrocarbons) released by industrial, agricultural and population growth. The Pearl River Delta (PRD) region, extending from the Hong Kong metropolitan area to the northwest, has been the most economically dynamic region of mainland China over the last two decades. The high levels of NO_x, SO_2, ozone and $PM_{2.5}$ observed in the PRD region over the past decade are believed to be associated with the rapid economic development (Zhang et al., 1998; Wang et al., 2003; Li et al., 2005a). As intermediate photochemical byproducts, hydroperoxides

can be used to test predictions by photochemical models by comparison with observed data (Jacob et al., 1996). Therefore, field studies of peroxides are needed urgently to provide valuable data for investigating the photochemical mechanisms in this region and to be included in photochemical models.

We present a novel dataset for speciated hydroperoxides measured at a rural site in PRD that has high mixing ratios of VOC and CO. The objectives of this study were to investigate the impact of chemical and physical processes on the mixing ratio of H_2O_2 and organic peroxides, to provide new field evidence of the existence of high mixing ratios of hydroperoxides in the upper planetary boundary layer (PBL), to examine the contribution of hydroperoxides to the formation of secondary sulfate and SOA, and ultimately to assess the value of hydroperoxide measurements for better understanding the mechanisms of secondary photochemical pollutions and to aid the development of more robust models.

2 Experimental

2.1 Measurement site

The observations are from the PRIDE-PRD'06 (Program of Regional Integrated Experiments of Pearl River Delta Region) Air Quality Monitoring Campaign that took place from the 3 to the 30 of July 2006 at Backgarden (23.5° N 113.0° E), a rural site in northern PRD, surrounded by 20 km^2 of forest and 2.7 km^2 of lake, located north of the central PRD and about 48 km northwest of Guangzhou, which is the capital city of Guangdong Province. In addition to the measurement of peroxides, all major trace gases (NO_x, NO_y, PAN, SO_2, CO, O_3, biogenic/anthropogenic VOC, etc.), aerosols (mass concentration, number concentration, chemical compositions), free radicals (OH, HO_2, RO_2) and meteorological parameters (temperature, wind direction, wind speed and relative humidity, rainfall) were monitored at this site by a number of groups.

2.2 Measurement method for hydroperoxides

The instrument for determining hydroperoxides was located in the uppermost room of a three story building. Ambient air was drawn by a vacuum pump through a 6 m Teflon tube (1/4 inch O.D.) extending 1.5 m above the roof of the building, so that the air samples were taken about 12 m above the ground. The air flow rate was 2.7 slm (standard liters per minute), controlled by a mass flow controller. The air residence time in the inlet tubing was less than 2 s, and there was no filter in the inlet system. The air samples were collected in a thermostatically controlled glass coil collector, at a temperature of around 10°C. The stripping solution, acidified 18 MΩ water (H_3PO_4, pH 3.5) was delivered into the collector by an HPLC pump (Agilent 1050) at a rate of 0.2 mL min^{-1} to collect hydroperoxides. The coil itself is about 30 cm long and the tube has an effective length of ∼100 cm and 2 mm I.D. (Sauer et al., 1999). The scrubbing coil is similar to that used in earlier studies (Lazrus et al., 1986; Neeb et al., 1997; Sauer et al., 1999, 2001; Grossmann et al., 2003; François et al., 2005).

The collection efficiency of the coil was determined as follows. First, vapor containing H_2O_2 and MHP was generated by a saturated vapor generator (Lind and Kok, 1986; Li et al., 2004). The air stream flowed over the thermostatically controlled quartz fiber membrane (15±0.2°C), which was saturated by the standard solution, at a rate of 0.2 slm. Lind and Kok (1986) demonstrated that the air stream rate should be less than 1 slm in order to ensure Henry's Law equilibrium. Second, additional pure air (2.5 slm) was added to the generated vapor of hydroperoxides via a three-port valve. Then the mixed air stream of standard gas of H_2O_2 and MHP was drawn into the scrubbing coil collector at a total flow rate of 2.7 slm under the conditions used for atmospheric measurement. Using a solution containing 2.4×10^{-3} M H_2O_2 and 3.5×10^{-6} M MHP, the levels of gaseous hydroperoxides in the standard gas were calculated to be ∼1 ppbv for H_2O_2 and ∼0.5 ppbv for MHP. The concentration of this standard gas was also determined using a Horibe tube in a cold trap of ethanol/liquid nitrogen at ∼ –90°C (Hewitt and Kok, 1991), for collection and for HPLC analysis (described

below). The standard gas concentration determined by the cold trap method was consistent with the concentration calculated by Henry's Law ($H_{H_2O_2}=1.8\times10^5$ M atm^{-1} and $H_{MHP}=5.7\times10^2$ M atm^{-1} at 28-8 K, Sander et al., 2003). After collection, the stripping solution was analyzed by HPLC. The collection efficiency of the coil was estimated using the ratio of the measured concentration and the known concentration of the standard gas, with ≥98% for H_2O_2 and ∼85% for MHP at 10°C. These values are in agreement with those of previous studies (Sauer et al., 1997, 2001; François et al., 2005). The heterogeneous decomposition of H_2O_2 and MHP in the coil was negligible under the experimental conditions, as proved by previous studies (Sauer et al., 1996, 2001).

After the sampled air passed through the coil collector, the stripping solution was removed from the separator using a peristaltic pump and immediately injected manually into the HPLC valve, from which 100 μL was analyzed by HPLC. Because of the lack of an auto-sampler for the HPLC analysis, the sample analysis was performed in a quasi-continuous mode with an interval of 20–60 min, and thus only a few samples were measured at night and in the early morning. Several rain samples were collected during a heavy shower using a glass funnel (diameter 10 cm) connected to a 5 m Teflon tube (1/8-inch O.D.), from the end of which the rain samples were collected and injected immediately into the HPLC column.

The HPLC was done with post-column derivatization using *p*-hydroxyphenylacetic acid (POPHA) and fluorescence detection. The basis of this method is to quantify the fluorescent dimer produced by the stoichiometric reaction of POPHA and hydroperoxides through catalysis (Gäb et al., 1985; Hellpointner and Gäb, 1989; Kurth et al., 1991; Lee et al., 1995; Sauer et al., 1996, 1997, 1999, 2001; Grossmann et al., 2003; François et al., 2005; Xu and Chen, 2005; Walker et al., 2006). The catalyst used in this study was Hemin (Xu and Chen, 2005; Chen et al., 2008). The mobile phase, controlled by the HPLC pump (Agilent, 1200) at a constant rate of 0.5 mL min^{-1}, was a H_3PO_4 solution at pH 3.5 (Sigma-Aldrich, 85% for HPLC). The hydroperoxides were separated in a 5 μM reversed-phase C_{18} HPLC column (4.6 mm×250 mm, ZORBAX, SB-Aq, Agilent), which was cooled to ∼2°C to stabilize the hydroperoxides. After separation, the eluate was introduced into a 3 m Teflon coil at 42(±1)°C for post-column derivatization. The fluorescent reagent, 8×10^{-6} M Hemin (Fluka) and 8×10^{-5} M POPHA (ACROS ORGNICS), was adjusted to pH 10–11 with NH_4Cl/NH_4OH buffer solution. The flow rate of the fluorescent reagent was 0.2 mL min^{-1}. The fluorescence signal of the biphenyl derivative formed in the derivatization reaction was determined at wavelengths of λ_{Ex}=315 nm and λ_{Em}=400 nm using a fluorescence detector (Agilent 1200).

Sample blanks were determined at least twice daily by measuring the stripping solution at the stripping solution outlet of the coil after stopping the air vacuum pump for 10 min. H_2O_2 was occasionally found in the blanks but only in trace amounts. Multipoint calibration of the HPLC for analysis of hydroperoxides was performed weekly with H_2O_2, MHP and EHP standard solution in the range of 1×10^{-8}~1×10^{-5} M, and single-point calibration was done three times a day with a mixing standard solution of H_2O_2, MHP and EHP. Organic hydroperoxides were identified by comparing the retention times with those of reference substances. The detection limit (d.l.), defined as three times the standard deviation of the analytical blanks, was 0.012 μMol L^{-1} using a 100 μL sampling loop. This corresponded to a d.l. of about 20 pptv for H_2O_2 and organic hydroperoxides in the gas phase under these sampling conditions.

H_2O_2 was purchased from Sigma-Aldrich (35%), and fresh solutions were prepared by serial dilution of the 0.35% stock solution. Methyl hydroperoxide and ethyl hydroperoxide were synthesized from H_2O_2 and dimethyl sufate or diethyl sulfate as described (Rieche and Hitz, 1929; Kok et al., 1995; Lee, et al., 1995). The hydroxymethy hydroperoxide (HMHP), 1-hydroxy-ethyl hydroperoxide (1-HEHP) were synthesized from aqueous H_2O_2 and formaldehyde or acetaldehyde (Rieche and Meister, 1935; Zhou and Lee, 1992; Lee et al., 1995). The concentrations of stock solutions and standard solutions were determined using $KMnO_4$ and $KI/Na_2S_2O_3$/starch every two weeks (Johnson and Siddigu, 1970; Mair and Hall, 1970). All reagents and standard solution were prepared with 18 MΩ Milli-Q water (Millipore), and were stored at 4°C in a refrigerator.

2.3 Measurement methods for other trace gases

HO_2 radicals were measured at the Backgarden site by a laser-induced fluorescence instrument, operated by Forschungszentrum Juelich (FZJ). Briefly, ambient air is sampled continuously into a low-pressure detection chamber, where HO_2 is chemically converted to OH by reaction with added NO. The resulting OH is then detected by laser excited fluorescence at a wavelength of 308 nm. The instrument is calibrated by using the quantitative photolysis of water vapour in synthetic air at 185 nm as a radical source. The accuracy of the measurements is estimated to be 20% for this campaign. Details of the instrument and its calibration can be found in Holland et al. (2003).

Semi-continuous measurements of WSOC were made by University of Tokyo (UT) using a particle-into-liquid sampler (PILS) followed by online quantification of TOC every 6 min using a total organic carbon (TOC) analyzer. Ambient aerosol was sampled at a flow rate of 16.7 L/min by the PILS, which used a steam saturator to grow the aerosol to sizes that can be collected by inertial impaction. The carbonaceous compounds in the liquid sample were then quantified online with the TOC analyzer. Details of the instrument can be found in Miyazaki et al. (2006).

The sulfate measurements were performed by the Aerodyne Aerosol Mass Spectrometer (AMS), operated by University of Tokyo (UT). The AMS can measure size-resolved chemical composition of ambient non-refractory (vaporized at 600°C under high vacuum) submicron aerosol for an integration time of 10 min. The AMS consists of a particle sampling inlet, a particle time-of-flight (PTOF) chamber, and a vaporizer/ionizer that is interfaced to a quadrupole mass spectrometer (QMS). Details of the instrument can be found in Takegawa et al. (2005).

The SO_2 was determined by Peking University (PKU) using SO_2 Analyzer (Thermo, Model 43C) with a time resolution of 1 min. The data of CO, O_3 and NO_x used in this study were obtained from the combined data set of PKU, UT and FZJ. During the period we discuss in this study, the CO was measured by a CO Analyzer (Thermo, Model 48C) with a time resolution of 1 min, operated by PKU, and a non-dispersive infrared absorption (NDIR) instrument with an integration time of 1 min (Model 48, TECO), operated by UT (details of the instrument described by Takegawa et al. 2006), and the O_3 was mainly measured by a O_3 Analyzer (Thermo, Model 49C) with a time resolution of 1 min operated by PKU. NO_x and NO_y were measured using a NO-O_3 chemiluminescence detector combined with a photolytic converter and a gold tube catalytic converter (Takegawa et al., 2006). NO_y compounds were catalytically converted to NO on the surface of a gold tube heated at 300°C. The photolytic converter system used for the NO_2 measurement was manufactured by the Droplet Measurement Technologies, Inc., USA.

3 Results and discussion

3.1 General observations

A total of 354 air samples were characterized using the scrubbing coil collector from the 19 to the 30 of July 2006 during the PRIDE-PRD'06 campaign. The major hydroperoxide present in the air samples collected at the Backgarden site was H_2O_2 with mixing ratios between below the detection limit (20 pptv) and 4.6 ppbv, and MHP with mixing ratios between <20 pptv (d.l.) and 0.8 ppbv. The organic peroxides BHMP and PAA were often detected, and HMHP, 1-HEHP and EHP were occasionally detected, but all these species were present at only several-decade pptv level under these experimental conditions. In order to calculate the mean of the observed mixing ratios, any value below the detection limit was treated as zero. With regard to all samples, the mean (and standard deviation) mixing ratios during the daytime (08:00–20:00 LT) were 1.26±1.24 ppbv for H_2O_2 and 0.28±0.10 ppbv for MHP. The mean values at night (20:00–02:00 LT) were 0.74±0.62 ppbv for H_2O_2 and 0.19±0.10 ppbv for MHP. The mixing ratios of H_2O_2 and MHP are in agreement with those reported in the literature (Hellpointner and Gäb, 1989; Hewitt and Kok, 1991; Das and Aneja, 1994; Watkins et al., 1995a, 1995b; Jackson and Hewitt, 1996; Sauer et al., 1997, 2001; O'Sullivan et al.

1999; Morgan and Jackson, 2002; Moortgat et al., 2002; Grossmann et al., 2003; Lee et al., 1993, 1995, 1998, 2000, 2008; François et al., 2005; Xu and Chen, 2005; Walker et al., 2006; Kim et al., 2007).

Temporal profiles of the H_2O_2 and MHP mixing ratios for the time of the campaign are shown in Fig. 2. The maximum mixing ratio of H_2O_2 and MHP was found on 19 July, and this will be discussed in detail later. On sunny days with low levels of NO_x and SO_2, H_2O_2 showed pronounced diurnal variations, with peak mixing ratios in the afternoon (12:00–18:00 LT) and low values at night and in the early morning. Sometimes, a second peak occurred in the evening between 20:00 and 02:00 LT. The diurnal variation of MHP was consistent with, but less pronounced than, that of H_2O_2. The general diurnal cycle of H_2O_2 observed at Backgarden was similar to that observed in earlier studies (Sauer et al., 2001; Grossmann et al., 2003). Over the 13 days of measurement, HMHP was detected in only a few samples; probably resulting from the heterogeneous decomposition of HMHP at glass surfaces during sampling (Neeb et al., 1997; Sauer et al., 2001).

Figure 3 depicts the hourly averaged mixing ratio profiles of H_2O_2 and MHP with the vertical bars showing the standard deviation of the measured values. A similar averaged diurnal profile for H_2O_2 has been reported (Das and Aneja, 1994; Sauer et al., 2001). The concentration of H_2O_2 began to rise in the morning (~10:00 LT) and reached a maximum mixing ratio at 13:00 LT. The factors responsible for the H_2O_2 diurnal variation are discussed in detail in Sect. 3.2.2. The level of H_2O_2 remains relatively high in the afternoon and the mixing ratio decreased slowly from sunset to 24:00 LT. The diurnal profile of MHP is largely coincident with that of H_2O_2 in the daytime, but remained at an almost identical level after sunset. This slower loss of MHP at night can be explained by its lower level of solubility ($H_{H_2O_2}/H_{MHP}$=~260, at 298 K, Sander et al., 2003).

With regard to the meteorological conditions and levels of hydroperoxides, three distinct periods could be distinguished. (i) At the beginning of the measurement, 19–21 July, days were sunny with slight breeze, and hydroperoxides exhibited high mixing ratios during the days. (ii) The second period, 23–26 July, was influenced by typhoon Kaemi, which came across most of the PRD but, in particular, the central and eastern parts, resulting in more heavily polluted conditions than normal in this region (Z. B. Yuan, 2007, personal communication). High levels of hydroperoxides were observed also on the 24 and 25 of July, two sunny days. (iii) During the last days of the campaign, 27–30 July, the local weather conditions were cloudy and rainy, and daytime values of hydroperoxides were low.

The low daytime average H_2O_2 values probably result from several factors, and the most important one is that the weak photochemical activity on cloudy days produces fewer HO_x radicals compared to sunny days, resulting in low-level production of hydroperoxides. Moreover, the high levels of NO_x will significantly suppress the formation of hydroperoxides by consuming their precursors, peroxy radicals. Additionally, efficient scavenging of H_2O_2 on wet surfaces (leaves and fog droplets) and water-covered aerosols, in particular with a high level of SO_2 and high relative humidity conditions, should partly account for the low levels of H_2O_2.

3.2 Photochemistry on sunny days

3.2.1 Pattern of hydroperoxides and their precursors

The meteorological conditions during 19–21 July at Backgarden can be treated as identical. On these three sunny days, the maximum temperature was 35°C, and the relative humidity decreased from ∼90% in the early morning to ∼60% at noon. After reaching a minimum level of ∼45% in the afternoon, relative humidity increased gradually until the next morning. The wind speed was steady at around 0–3 m/s. The wind direction on 19 July turned clockwise via southeast in the morning to southwest at noon and back to southeast gradually in the late afternoon, and then remained southeast during the night. A similar pattern of wind direction was observed on the next two days.

The maximum mixing ratio of H_2O_2 and MHP was measured on 19 July, a sunny day with a slight breeze. As Fig. 4 shows, the concentration of NO_x stayed very high from

night to the early morning, with 36 ppbv at 08:15 LT. The high NO_x mixing ratio might have been caused by the accumulation of surface emission below the nocturnal inversion layer. After 08:15 (LT), the concentration of NO_x decreased rapidly to ∼8 ppbv at 10:30 LT, and remained at a relatively low level (1∼3 ppbv) until sunset. The rapid drop of NO_x probably resulted from the growing height of the mixing layer and changes in the wind direction. On the morning of 19 July, the wind direction turned clockwise via northeast (06:00 LT) to east (08:00 LT), and then to south (09:30 LT). The mixing ratio of H_2O_2 began to increase markedly at 08:45 and reached 2.8 ppbv at 10:30 LT, which is consistent with the sudden drop of NO_x detected, and the hydroperoxides showed a high level during the daytime. A similar diurnal trend of NO_x was observed during the daytime on 20–21 July. Chin et al. (1994) suggested that a NO_x/NO_y ratio of <0.3 could be used to determine when an air-mass can be described as photochemically aged. The NO_x/NO_y ratio was <0.3 between 12:00 and 17:00 LT during the three days, indicating that the air could be described as photochemically aged. This classification was supported also by the ratio of toluene/benzene. Li et al. (2005b) suggested that a value of toluene/benzene below 0.5 is indicative of photochemically aged air due to the shorter atmospheric lifetime of toluene compared to benzene. Therefore, the high levels of hydroperoxides in this period were thought to be due to a combination of photochemically aged air with very high levels of HO_x, relatively low levels of NO_x (compared to the other days during the observation at this site), and little surface deposition. This will be discussed in detail in Sect. 3.2.2.

As described previously, the formation of hydroperoxides can be represented by reactions (1) and (2) (k_1 and k_2 are taken from Sander et al. (2003), at 298 K):

$$HO_2 + HO_2 \xrightarrow{k_1} H_2O_2 + O_2 \quad k_1 = 1.5 \times 10^{-12} cm^3 molecule^{-1} s^{-1} \tag{1}$$

$$HO_2 + HO_2 + (M) \xrightarrow{k} H_2O_2 + (M)$$

M is air, the calculation of k should take into account the pressure dependence and the temperature dependence. For systems containing water vapor, the water vapor dependence expressed by the multiplicative factor: $1+1.4\times10^{-21}[H_2O]\exp(2200/T)$ should also be included. The expression for k is described in detail by Stockwell (1995).

$$CH_3O_2 + HO_2 \xrightarrow{k_2} CH_3OOH + O_2 \quad k_2 = 5.2\times10^{-12}\,\text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \tag{2}$$

However, the NO reaction with peroxy radicals will compete with the formation of hydroperoxides (k_3 and k_4 are taken from Sander et al. (2003), at 298 K):

$$HO_2 + NO \xrightarrow{k_3} OH + NO_2 \quad k_3 = 8.1\times10^{-12}\,\text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \tag{3}$$

$$CH_3O_2 + NO \xrightarrow{k_4} CH_3O + NO_2 \quad k_4 = 7.7\times10^{-12}\,\text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \tag{4}$$

Hence, the atmospheric lifetime of HO_2 radicals can be estimated as:

$$\tau_{HO_2-HO_2} = \frac{1}{k_1\,[HO_2]} \tag{5}$$

$$\tau_{HO_2-CH_3O_2} = \frac{1}{k_2\,[CH_3O_2]} \tag{6}$$

$$\tau_{HO_2-NO} = \frac{1}{k_3\,[NO]} \tag{7}$$

$$\tau_{CH_3O_2-NO} = \frac{1}{k_4\,[NO]} \tag{8}$$

where $\tau_{HO_2-HO_2}$, $\tau_{HO_2-CH_3O_2}$ and τ_{HO_2-NO} are the lifetimes of HO_2 radicals due to the self-recombination reaction, CH_3O_2 reaction and NO reaction, respectively; $\tau_{CH_3O_2-NO}$ is the lifetime of CH_3O_2 radicals due to the NO reaction. $[HO_2]$, $[CH_3O_2]$ and [NO] are the concentrations of HO_2, CH_3O_2 and NO, respectively.

Equations (1)–(4) can be used to estimate if the formation of hydroperoxides is dominant compared with the NO reaction. In the clean atmosphere, the typical concentration of HO_2 radicals is $\sim1\times10^8$ molecule cm^{-3}; thus, when the concentration of NO is >100 pptv, the reaction of NO with HO_2 and RO_2 will suppress the production of H_2O_2 and MHP substantially, since the reactions of NO with peroxy radicals are faster than recombination reactions of peroxy radicals (Lee et al., 2000). Moreover, it is calculated that an NO mixing ratio below 10 pptv is needed for H_2O_2 to dominate over the reaction between HO_2 and NO (Reeves and Penkett, 2003; Crutzen and Zimmermann, 1991; Finlayson-Pitts and Pitts, 1986). Such low concentrations of NO can exist only in very remote regions of the troposphere. However, on the basis of Eq. (1), this conclusion should be re-evaluated for a region with very high levels of HO_2 radicals.

At Backgarden, the average NO mixing ratio on 19–21 July was a relatively low value, ~80 pptv, in the afternoon (14:00–18:00 LT). However, on 19–21 July the average NO mixing ratio at 10:30–14:00 LT was relatively high, ~280 pptv, and at the same time the levels of H_2O_2 and MHP increased rapidly up to almost the maximum value of the day. This value of NO (280 pptv) was much higher than those reported for earlier studies (Lee et al., 2000; Reeves and Penkett, 2003). Hence, our measurements represent a novel dataset showing that hydroperoxides can be formed and exhibit high mixing ratios in the daytime under polluted air with relatively high mixing ratios of NO_x. This situation may be attributed to the exceptionally high mixing ratio of HO_2 radicals ($\sim2\times10^9$ molecule/cm^3 at noon) produced by oxidation of VOC and CO at Backgarden.

3.2.2 Kinetics analysis

In general, $j(NO_2)$ can be used as an indicator for photochemically effective radiation. At Backgarden, $j(NO_2)$ usually began to rise after 06:00 (LT), reached maximum values of $\sim8\times10^{-3}\,\text{s}^{-1}$ at noon and then returned to near-zero after 19:00 (LT) (personal communication by B. Bohn, Forschungszentrum Juelich). During 19–21 July, the maximum mixing ratios of H_2O_2 were observed during the daytime, and the diurnal variation of H_2O_2 was generally similar to that of $j(NO_2)$, but the peak values were 2~3 h later. Generally, the photo-oxidant formation began about 3 h after the increase of radiation. The peak time of H_2O_2 approached that of O_3 on 19 and 20 July, and the diurnal profiles of these two species were similar. Additionally, peroxy acetic acid (PAA), which is produced mainly by photo-oxidation of acetone and PAN, was often detected on 19–21 July. On the basis of this evidence, we can infer that H_2O_2 and MHP were produced, to a large extent, in the daytime by the local photochemical process during the three days.

Even more direct evidence of the photochemical formation of hydrogenperoxide can be obtained from the diurnal profiles of HO_2, which were also measured at Backgarden. The HO_2 concentration can be used to calculate the chemical production rate of H_2O_2. The mixing ratios of HO_2 and H_2O_2 measured on July 21 are shown in Fig. 5. The mixing ratios of H_2O_2 and HO_2 are almost zero at the high concentration of NO_x before 09:30 (LT). The sharp increase of H_2O_2 at about 09:45 (LT) on July 21 coincides with the decrease of the NO_x mixing ratio, which might be explained by vertical exchange. During 10:00–12:00 LT, H_2O_2 continued to rise at a rate of ~0.81 ppbv h^{-1}, and the chemical production rate of H_2O_2 was ~0.74 ppbv h^{-1}, as determined from the HO_2 concentration of ~8.9×10^8 molecule cm^{-3}. The calculation adopts the expressions recommended by Stockwell (1995), and the HO_2 concentration and temperature uses the average value during the period, resulting in a rate coefficient of 6.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 60% relative humidity. This indicates that most of the H_2O_2 increase was produced by in situ formation and the rest might be attributed to the net effect of vertical mixing. As shown in Fig. 5, the diurnal cycles of HO_2 and H_2O_2 were, in general, consistent in the afternoon until 17:00 (LT); after that, the level of H_2O_2 had a weak correlation with that of HO_2. It is worth noting that the relative humidity rose rapidly after 17:00 LT, while the concentration of NO remained low (~30 pptv) in the evening of 21 July.

The decrease of H_2O_2 during the late afternoon until the night may be attributed to the following reasons. First, considering the high solubility of H_2O_2 (Lind and Kok,

1994; O'Sullivan et al., 1996), the observed low levels can be explained by increased relative humidity (~80% at 21:00 LT), which results in greater wet deposition of H_2O_2 at night than during the daytime. Secondly, the dry deposition of hydroperoxides on the Earth's surface will become very pronounced under a shallow inversion and at a low wind speed. The wind speed in the evening on 21 July was ~1 m/s; therefore, dry deposition on the surface might have acted as an important sink for loss of H_2O_2. Moreover, Walcek (1987) and Wesley (1989) have found that the deposition rate of H_2O_2 over trees is much higher than in the free troposphere. Hence, the low mixing ratios of H_2O_2 might be due, in part, to the deposition on the leaves of the dense forests surrounding the observation site. Furthermore, when the temperature decreased during the night, Henry's Law constant of H_2O_2 will increase, resulting in a removal of H_2O_2 from the gas phase into the liquid phase. As a result, the vast lake adjacent to the observation site might be substantially responsible for the decrease of H_2O_2.

3.2.3 Impact of local meteorology on hydroperoxides

The two sunny periods discussed here suggests that the hydroperoxide formation at Backgarden is, to a large extent, a local phenomenon. High levels of hydroperoxides were observed in the two sunny periods between 19–21 and 24–25 July. The mixing ratios of hydroperoxides were similar in the two periods. Moreover, the diurnal variation of H_2O_2 showed a positive correlation with O_3 on 24 July, as shown in Fig. 4, with the peak time of H_2O_2 2–3 h later than that of O_3. A ratio of toluene/benzene of <0.5 was observed between 12:00 LT on 24 July to 21:00 LT on 25 July, with a few exceptions in the early morning of 25 July. This indicates that during that time the air at Backgarden influenced by the typhoon front was photochemically aged. All the evidence indicates that local photochemical activity contributed substantially to the levels of hydroperoxides during 24 and 25 July.

It is worth noting that the dominant wind directions in the two sunny periods were opposite. As mentioned previously, southeasterly winds prevailed at the observation site during 19–21 July. On 24 and 25 July, the wind direction at Backgarden was northerly and veered to northwesterly in the afternoon, consistent with that of back trajectories obtained from NOAA (www.arl.noaa.gov). The wind speeds measured during the daytime of these two periods were similar, at ~2 m/s, ensuring transport of air masses over distances ~30 km between sunrise and the maximum observed photo-oxidant values. This suggests that the levels of hydroperoxides at Backgarden were not influenced by transport at low wind speed.

Thus, much of the variation of hydroperoxide mixing ratios observed at Backgarden on these sunny days can be attributed, to a large extent, to the local photochemical drive.

3.3 Rain

The heavy shower that started at 21:20 LT on 25 July and lasted for 40 min was brought by the typhoon Kaemi. At 17:00 LT, the wind direction turned from north to northwest, and the mixing ratios of NO_x, SO_2 and CO began to rise, reaching 19 ppbv, 9 ppbv and 1.6 ppmv, respectively, at 21:00 LT, while O_3 decreased from 54 ppbv to 8 ppbv, as shown in Fig. 4. At the same time, the levels of hydroperoxides decreased rapidly, i.e., H_2O_2 went from 3.2 ppbv to 0.9 ppbv and MHP went from 0.6 ppbv to 0.3 ppbv. These changes were interrupted at 21:20 LT when there was a heavy shower at Backgarden. When the rain began to fall, the temperature at ground level was 302 K. The shower lasted for ~40 min with lightning activity. During the shower, three rainfall samples were collected and analyzed immediately. The maximum concentration of H_2O_2 in the rain samples, 21 μ Mol/L, was detected at the beginning of the shower. This concentration is within the range reported for earlier studies (Hellpointner and Gäb, 1989, Jacob et al., 1990; Hewitt and Kok, 1991; Sauer et al., 1997; Morgan and Jackson, 2002). Moreover, MHP, which is seldom observed in rain samples (Hellpointner and Gäb, 1989; Pena et al., 2001; Reeves and Penkett, 2003), was detected in the rain samples at Backgarden at a concentration of 1.1 μMol/L. This value may represent the concentration of MHP in cloud water. If we assume that the MHP value in the gas phase at the height of the cloud base was the same as that detected at ground level, ~0.5 ppbv, the equilibrium

concentration of MHP in cloud water is estimated to be 0.2 μ M, on the basis of Henry's Law (H_{MHP}=4.16×10^2 M atm^{-1}, 293 K, Sander et al., 2003). This estimated value is much smaller than the concentration of MHP detected in the rainwater, which implies a higher gas-phase level of MHP in the clouds compared to that at ground level. Similarly, this higher concentration above PBL (1~2 km) can be estimated by Henry's Law. The ambient temperature will decrease 6~7 K when the altitude increases by 1 km; thus, the temperature at the height of the cloud base can be estimated to be ~293 K, while the temperature at ground level was 302 K. According to the concentration of MHP detected in the rain (1.1 μMol/L), the gas-phase MHP mixing ratio above PBL was ~2.6 ppbv. This estimated value is slightly higher than those reported for earlier field studies in which MHP was detected directly by aircraft (O'Sullivan et al., 1999; Lee et al., 2000). MHP may be of great importance in the redistribution of OH radicals along with the driving force of atmospheric chemistry (Wennberg et al., 1998; Cohan et al., 1999; Ravetta et al., 2001; Mari et al., 2000). Our measurement may be new evidence for the existence of high mixing ratios of MHP at the height of the PBL.

The levels of hydroperoxides after the shower lend support to the deduction that high mixing ratios of hydroperoxides occur in the PBL. H_2O_2 and MHP exhibited relatively high mixing ratios of 2.1 ppbv and 0.64 ppbv, respectively, immediately after the shower; meanwhile, the mixing ratios of NO_x, SO_2 and CO decreased to relatively low values due to the dilution and scavenging effects, as shown in Fig. 4. The mixing ratios of hydroperoxides after the shower were even higher than they were before the shower. Considering the much higher solubility of H_2O_2 than that of NO_x, SO_2 and CO, we suggest that vertical convection might contribute significantly to the increased H_2O_2 and MHP mixing ratios, for the following two reasons. First, the air mass in the upper boundary layer may be carried down to the land surface when rain falls. As a result, the gas-phase H_2O_2 above PBL that was not washed out by the shower might affect the mixing ratio at low altitudes. Second, the falling rain and rainwater on the ground (e.g. on the leaves of plants) might release H_2O_2 and MHP into the gas phase during and after the shower, because of the decrease of Henry's Law constants due to the increase of temperature with descending altitude. In addition, owing to the low level of solubility and its estimated 2–3 days atmospheric lifetime (Cohan et al., 1999; Wang and Chen, 2006), a fraction of the increased MHP might be introduced partly by the advection of typhoon from other regions. Moreover, although the measurement of VOC was interrupted in the hours following the shower, the low mixing ratio of alkenes (∼2 ppbv) at around 21:20 LT indicated that the ozonolysis alkenes might have a minor impact on the level of hydroperoxides during the shower.

Overall, this measurement of hydroperoxides during the shower may provide evidence for the high mixing ratio of MHP above the boundary layer. This mixing ratio of MHP might potentially influence the redistribution of HO_x and RO_x radical in the PRD on a regional scale.

3.4 Formation of hydroperoxides by ozonolysis

The ozonolysis of alkenes (e.g. isoprene, terpenes, ethene, propene and isobutene) can produce a variety of peroxides (Gäb et al., 1985, 1995; Becker et al., 1990, 1993). It is proposed that ozonolysis proceeds by the initial insertion of the ozone into the double bond forming a primary ozonide, and decomposes to form excited Criegee intermediates (ECI) $[R_1R_2COO]^*$ and a carbonyl compound (Gäb et al., 1985). ECI are biradicals with excess energy, and some of them will become stabilized Criegee intermediates (SCI) R_1R_2COO by interaction with the medium, and the SCI can react further to produce hydroperoxides. Recent laboratory studies have revealed that $R_1R_2C(OH)OOH$ can be formed by the reaction of SCI with water vapor (Horie et al., 1994; Neeb et al., 1997; Sauer et al., 1999; Valverde-Canossa et al., 2001). This $R_1R_2C(OH)OOH$ decomposes primarily to H_2O_2 and a carbonyl compound R_1COR_2, as shown in the following reactions (R_1 and R_2 are alkyl groups):

$$R_1R_2COO + H_2O \rightarrow R_1R_2C(OH)OOH \quad (9)$$

$$H_2COO + H_2O \rightarrow HOCH_2OOH \quad (R_1 = H, R_2 = H) \quad (10)$$

$$R_1R_2C(OH)OOH \rightarrow R_1COR_2 + H_2O_2 \quad (11)$$

The other ECI undergoes a series of reactions, yielding products such as HCHO, HCOOH, CO, CO_2, H_2O and radical species including OH, HO_2, and organic radicals (Donahue et al., 1998; Neeb and Moortgat, 1999; Mihelcic et al., 1999; Kroll et al., 2001). It is suggested that the ozonolysis of alkenes might be an important source of OH, HO_2 and organic radicals at night or under conditions of low solar intensity (Paulson and Orlando, 1996; Bey et al., 1997; Ariya et al., 2000).

There is some evidence that H_2O_2 and MHP were formed in the evening. As shown in Fig. 6, a high H_2O_2 mixing ratio was detected after sunset (19:20 LT) on July 24; in particular, a second peak (∼1.9 ppbv) was observed during the evening. Relatively high mixing ratios of alkenes (∼8 ppbv), particularly isoprene (∼5 ppbv), were detected during the evening on 24 July, compared to the other nights. The mixing ratio of H_2O_2 at 21:00 LT was about half of the maximum value observed during the daytime. However, the level of HO_2 at this time was $\sim 3\times10^8$ molecules cm^{-3}, only ∼13% of the maximum value observed at midday, as shown in Fig. 6. This high level of H_2O_2 production cannot be attributed to only the recombination of HO_2 radicals, suggesting that the formation via the ozonolysis of alkenes under moist atmospheric conditions (70% relative humidity) contributes substantially to the production H_2O_2 during the evening. Further evidence for this pathway comes from the fact that $HOCH_2OOCH_2OH$ (BHMP) was observed for a considerable length of time only during the night of 24 July. The apparent precursor of BHMP is HMHP (Gäb et al., 1985), which is a unique product of the ozonolysis of exocyclic biogenic alkenes (Valverde-Canossa et al., 2001). HMHP is formed by CH_2OO biradicals, which are produced in the ozonolysis of terminal alkenes, as shown in reaction (10), while the formation of BHMP can be expressed by Eq. (7):

$$HOCH_2OOH + HOCH_2OOH \rightarrow HOCH_2OOCH_2OH + H_2O \quad (12)$$

Therefore, the reaction of alkenes with O_3 can be suggested as a source of hydroperoxides at night at the Backgarden site. Grossmann et al. (2003) proposed that the ozonolysis of alkenes was a source of H_2O_2 at night at Pabstthum, Germany.

It is worth noting that MHP had a diurnal profile similar to that of H_2O_2 in the evening at Backgarden, and MHP also exhibited a second peak 0.4 ppbv at night on July 24. This level of MHP at night was much higher than those reported for other continents (Hellpointner and Gäb, 1989; Jackson and Hewitt, 1996; Sauer et al., 2001; Grossmann et al., 2003; Walker et al., 2006).

3.5 Hydroperoxide contribution to aerosols

3.5.1 Role of hydroperoxides in the formation of secondary sulfate

Atmospheric aerosols are responsible for the deterioration of air quality in industrialized areas and adversely affect human health and welfare. A major component of aerosols in North America, Europe, and Asia is secondary sulfate resulting from the atmospheric oxidation of anthropogenically emitted sulfur dioxide (SO_2) (US Environmental Protection Agency, 2001). Therefore, the oxidants and oxidation processes involved in the formation and growth of secondary sulfate are important subject in need of further study, especially when taking into account the long-range transport of anthropogenic sulfate aerosols (Perry et al., 1999). During the PRIDE-PRD'06 campaign, sulfate present in the aerosol phase was determined to be a major component, 10~60%, of $PM_{2.5}$ mass (S. Guo, 2008, personal communication, Peking University). The main oxidation process for SO_2 in the atmospheric gas phase is its reaction with OH radicals, see Eqs. (8)–(10) (Finayson-Pitts and Pitts, 1986):

$$SO_2 + OH \xleftrightarrow{M} HOSO_2 \quad (13)$$

$$HOSO_2 + O_2 \xrightarrow{M} HO_2 + SO_3 \quad (14)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (15)$$

$$-d[SO_2]/dt = k_{13}^{bi}[OH][SO_2] \quad (16)$$

k_{13}^{bi}=1.3×10^{-12} cm^3 molecule^{-1} s^{-1} (effective bimolecular rate constant) (Atkinson et al., 2004).

However, it is suggested that the aqueous phase reaction with H_2O_2 and O_3 is the main route for SO_2 oxidation. The aqueous-phase oxidation with H_2O_2 accounts for 60~80% of the total oxidation of SO_2 in the atmosphere, especially when the pH is <4.5 (Penkett et al., 1979; Calvert et al., 1985). Organic hydroperoxides such as MHP, HMHP and PAA are also able to oxidize SO_2 (Lind et al., 1987; Zhou and Lee, 1992). At the pH range of atmospheric interest (pH=2–7) most of the S(IV) species is in the form of the bisulfite ion (HSO_3^-). Reactions leading to the formation of sulfuric acid by hydroperoxides in the aqueous phase are as follows (Hoffmann and Edwards, 1975):

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \quad (17)$$

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O \quad (18)$$

$$R'_a = -d[S(IV)]/dt = k_{19}[H^+][H_2O_2][S(IV)] \quad (Ms^{-1}) \quad (19)$$

$$R'_a = 10^{-6}LR_a \quad (mol(L\ of\ air)^{-1}s^{-1}) \quad (20)$$

$$HSO_3^- + CH_3OOH + H^+ \xrightarrow{k_{21}} SO_4^{2-} + 2H^+ + CH_3OH \quad (21)$$

$$R_{21} = k_{21}[H^+][CH_3OOH][HSO_3^-] \quad (22)$$

$$HSO_3^- + CH_3C(O)OOH + H^+ \xrightarrow{k_{23}} SO_4^{2-} + H^+ + CH_3COOH \quad (23)$$

k_{19}=7.5±1.6×10^7 M^{-1} s^{-1} at 298 K, k_{21}=1.7±0.3×10^7 M^{-2} s^{-1} at 291 K, (Seinfeld and Pandis, 1998), L is the liquid water content (g H_2O/m^3 air)

While the total amount of dissolved S(IV) always exceeds that predicted by Henry's Law for SO_2 alone, and is enhanced at high pH values, the reaction of H_2O_2 with S(IV) is catalyzed by H^+ ions and is faster at low pH. Therefore, the rate of S(IV) reaction with H_2O_2 is practically independent of pH over the pH range of atmospheric interest (Schwartz et al., 1984). Similarly, the reaction of HSO_3^- with MHP is independent of pH. The oxidation of S(IV) to S(VI) by H_2O_2 in the aqueous phase is so fast that it can deplete the limiting compound within 1 h at pH<4.5 (Kelly et al., 1985). Considering the rapid loss of H_2O_2 into the aqueous phase due to its high Henry's Law coefficient, we propose that H_2O_2 may contribute significantly to the formation of sulfate (SO_4^{2-}) on droplets and aerosols covered by a water-soluble layer.

Evidence of SO_4^{2-} formation by H_2O_2 oxidation was seen on 21 July, as shown in Fig. 7. Between 13:30 and 15:30 LT, the mixing ratio of NO_x, SO_2 and especially CO varied slightly, the wind speed remained constant at $\sim 2\,m\,s^{-1}$ and the wind direction was southwesterly. Therefore, although it is well recognized that the sulfate can be transported to long distance (Perry et al., 1999), the transport might have a minor effect on the concentration of sulfate at the observation site during the above two-hour period. The high mixing ratio of H_2O_2 lasted from midday to the afternoon, while SO_2 displayed relatively low mixing ratios but increased slightly after midday. Meanwhile, the concentration of sulfate in the aerosol phase increased at a rate of $\sim 1.7\times10^{-11}\,mol\,m^{-3}\,s^{-1}$ between 13:30 and 15:30 LT. During this time, the relative humidity was ~50%, and we used $8.0\times10^{-4}\,g\,H_2O/m^3$ air as a general estimate of liquid water content in the ground-level air mass. Considering the aerosols in PRD region was generally acidic (M.-Q. Huo, 2008, personal communication, Peking University), we estimate the pH of the aerosols to be 4~5. On the basis of the average measured concentrations, with 1.0×10^7 molecule cm^{-3} for OH, 6.5 ppbv for SO_2, 2.8 ppbv for H_2O_2 and 50 ppbv for O_3, the sulfate production rate is $1.4\times10^{-12}\,mol\,m^{-3}\,s^{-1}$ in the aqueous phase (using Eqs. 19 and 20) and $3.5\times10^{-12}\,mol\,m^{-3}\,s^{-1}$ in the gas phase (using Eq. 16), resulting in a combined sulfate production in both phases of $\sim 4.9\times10^{-12}\,mol\,m^{-3}\,s^{-1}$. This estimated sulfate production is much smaller than the measured value of $1.7\times10^{-11}\,mol\,m^{-3}\,s^{-1}$, which indicates that other processes are responsible for the missed source of sulfate. It is worth noting that the calculated production of sulfate mentioned above includes only the production in the gas phase

and in the aqueous bulk of droplets. The heterogeneous chemistry on the surface of droplets and aerosols is potentially important (Li et al., 2006, 2007; Ammann and Pöschl, 2007; Pöschl et al., 2007; Chen et al., 2008), but it is not taken into account in the above estimation. Jayne et al. (1990) observed that the uptake of SO_2 into water droplets was faster than predicted on the basis of the known kinetics in bulk solution, and they suggested that a surface complex was formed between SO_2 and H_2O at the interface. Vácha et al. (2004) suggested that the concentration of H_2O_2 is increased in the interfacial region by ~50% compared to the bulk. Chung et al. (2005) pointed out that salts containing ammonium ions were found to increase the solubility of H_2O_2 by up to a factor of two compared to pure water. Hasson and Paulson (2003) found that the concentration of H_2O_2 within aerosols was of the order of 10^{-3} M, which is one order of magnitude higher than the expected concentration based on the solubility of H_2O_2 in liquid water ($\sim 1\times10^{-4}$ M). Moreover, Chen et al. (2008) recommended that the interfacial reaction should be taken into account in the generalized aqueous phase especially for a rapid reaction. Combining all these intriguing hints with our estimation, we suggest that the surface heterogeneous phase reaction, here, the heterogeneous reaction of SO_2 with H_2O_2 might make a substantial contribution to sulfate production. Clearly, the mechanism, kinetics parameters and yield of sulfate formation regarding the heterogeneous reactions need further investigation.

Recent studies have revealed that the enhanced acidity of the aerosol can catalyze particle-phase heterogeneous reactions of atmospheric organic carbonyl species (Jang et al., 2002, 2003; Iinuma et al., 2004). The reactions of SO_2 with hydroperoxides produce sulfate, and provide hydrogen ions continuously for heterogeneous reaction systems.

3.5.2 Contribution to the formation of secondary organic aerosol (SOA) in aerosols

SOA formed through oxidation of atmospheric VOC contributes to the global aerosol burden through both biogenic and anthropogenic precursors. The biogenic fraction of SOA contributes the most, with estimates varying between $8\,Tg\,yr^{-1}$ and $40\,Tg\,yr^{-1}$

(Penner et al., 2001). Recent laboratory studies have revealed that acid-catalyzed multiphase reaction of isoprene and its gas-phase oxidation product with hydrogen peroxide lead to the formation of SOA (Claeys et al., 2004; Böge et al., 2006; Kroll et al., 2006). This new route may explain the formation of water-soluble organic compounds (WSOC), which include hydroxyl and/or carboxyl functional groups and represent a considerable fraction of the SOA (Saxena and Hildemann, 1996).

Some evidence from the PRIDE-PRD'06 study indicates that a negative correlation might exist between the observed hydroperoxides and the concentration of WSOC. Figure 8 shows the measured concentrations of H_2O_2 and WSOC, and it can be seen that the diurnal variations of the two kinds of species are generally opposite.

It is generally accepted that the formation of SOA from biogenic hydrocarbons emitted by terrestrial vegetation is via gas-phase photochemical reactions followed by gas-to-particle partitioning (Seinfeld and Pandis, 1998). In the atmosphere, hydroperoxides and WSOC are competitive in their formation reactions, involving the intermediates R_1R_2COO and HO_2 radicals. Additionally, WSOC may be produced by multiphase acid-catalyzed oxidation with hydrogen peroxides as reported (Claeys et al., 2004; Böge et al., 2006; Kroll et al., 2006). Thus, a negative correlation of atmospheric hydrogen peroxide with aerosol-phase WSOC can be expected to some extent. In fact, the laboratory study revealed that the aqueous-phase ozonolysis of isoprene and its gas-phase oxidation product may serve as a potentially important route for the formation of oxidants, including H_2O_2 (Chen et al., 2008). The field evidence indicated that the sampled particles are capable of generating H_2O_2 in aqueous solution (Arellanes et al., 2006). Although it is difficult to distinguish quantitatively the contribution of gas-phase H_2O_2 and H_2O_2 generated in aqueous phase, our measurements provide evidence that atmospheric H_2O_2 contributes substantially to the formation of WSOC and a negative correlation might exist between the two kinds of species, as shown in Fig. 8.

In addition to H_2O_2, organic hydroperoxides, especially HMHP and MHP, may contribute substantially to the formation of WSOC. As mentioned above, HMHP can de-

compose to H_2O_2 and formaldehyde in the aqueous phase (O'Sullivan et al., 1996; Chen et al., 2008), which can subsequently participate in the formation of WSOC in the form of H_2O_2. It has been shown that the concentrations of H_2O_2 and MHP are similar in many parts of the atmosphere (Reeves and Penkett, 2003). Although the Henry's Law constant of MHP in pure water is much lower than that of H_2O_2, the role of MHP in the atmospheric aqueous phase may be much more important than that estimated by its Henry's Law constant in pure water. It is worth noting that formaldehyde was found in the aerosol at concentrations 1000-fold higher than the equilibrium concentration calculated only from its gas-phase formaldehyde and aqueous aerosol (Klippel and Warneck, 1978). This unexpected partitioning may be because formaldehyde in the aqueous aerosol is complexed with some soluble species (Facchini et al., 1992). The Henry's Law constant of formaldehyde obtained in this case is usually called its effective Henry's Law constant. However, to our knowledge, a similar study for enhanced solubility of MHP in the aqueous phase has not been reported. Considering the potential importance of MHP in the aqueous-phase reaction, its effective Henry's Law constant in solutions regarding real atmospheric conditions needs further study.

In summary, hydroperoxides play an important role in the formation of secondary sulfate and organic aerosols. First, hydroperoxides oxidize SO_2 into sulfate aerosols and simultaneously produce hydrogen ions. Second, with the increase of hydrogen ions derived from the above reaction, hydroperoxides will effectively oxidize organic compounds into WSOC by acid-catalyzed heterogeneous reactions. Third, the formation of WSOC will increase the hygroscopicity of aerosols, which in turn results in an increase of SO_2 oxidation by increasing the aqueous phase. Therefore, hydroperoxides serve as an important link between sulfate and organic aerosols. Such a link needs further study and should be considered in current atmospheric models.

4 Conclusions

Atmospheric H_2O_2 and organic hydroperoxides were measured for 13 days during the PRIDE-PRD'06 campaign at Backgarden, a rural site located 48 km north of Guangzhou. H_2O_2 and MHP were the dominant hydroperoxides present in the air with a maximum mixing ratio of 4.6 ppbv for H_2O_2 and 0.8 ppbv for MHP. BHMP, PAA, HMHP, 1-HEHP and EHP were detected occasionally. H_2O_2 exhibited the maximum mixing ratio mainly between 12:00 and 18:00 LT on sunny days and low values at night and in the morning. Sometimes a second peak was observed during the evening (20:00–02:00 LT), which might be produced by the ozonolysis of alkenes. The diurnal variation of MHP was generally consistent with that of H_2O_2 but less pronounced. The estimation for the H_2O_2 formation rate from HO_2 recombination indicates that in the morning most of the H_2O_2 was formed through local photochemical activity, and vertical mixing might be a source. It was noteworthy that high levels of hydroperoxides were found in polluted air with a high mixing ratio of VOC and CO. The high level of HO_2 radicals and the low level of NO detected simultaneously in this region in the day may effectively support the production of hydroperoxides. High concentrations of H_2O_2 and MHP were detected in samples of rain collected during a shower when a strong typhoon passed through the observation site. The estimation using Henry's Law indicates that a considerably high mixing ratio of MHP resided above the boundary layer and might further influence the redistribution of HO_x and RO_x radicals in the PRD region. Evidence was found that hydroperoxides, in particular H_2O_2, contributed considerably to the formation of aerosol-phase sulfate via the aqueous-phase oxidation, and heterogeneous reactions may contribute substantially to the concentration of sulfate measured at the site. Furthermore, the results suggested that hydroperoxides may contribute substantially to the formation of WSOC, as indicated by the fact that their diurnal variations exhibited a negative correlation. This provides evidence gathered in the field to support the importance of hydroperoxides in the formation of SOA found in laboratory studies. We suggest that hydroperoxides serve as an important

link between sulfate and organic aerosols. This link needs further study and should be considered in current atmospheric models.

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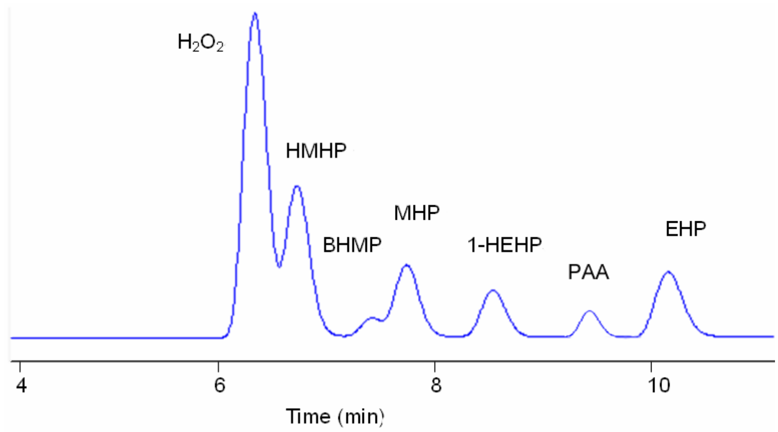

Fig. 1. HPLC chromatogram of a mixture of hydroperoxides showing separation and retention times.

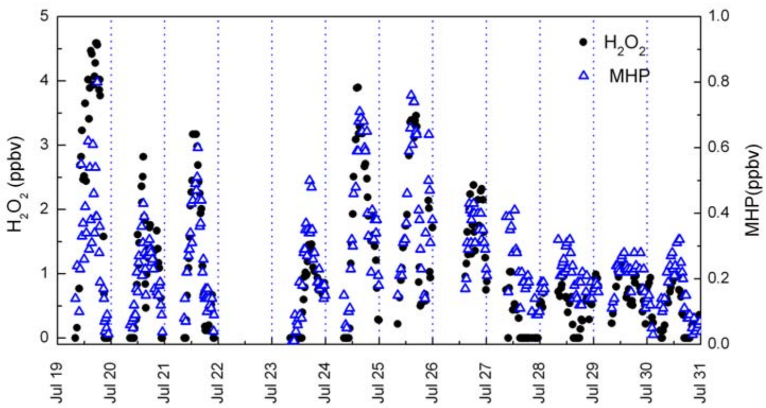

Fig. 2. Temporal profiles of atmospheric H_2O_2 and MHP mixing ratios from 19 to 30 July 2006 at Backgarden.

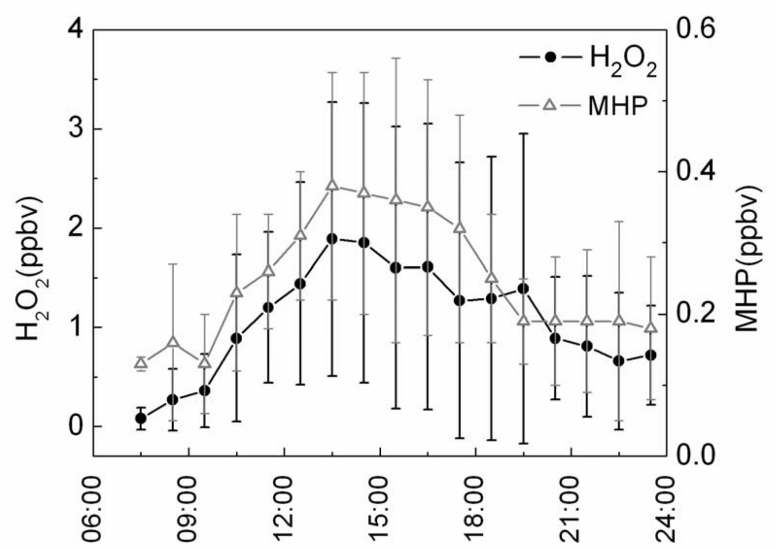

Fig. 3. Hourly averaged diurnal cycle for H_2O_2 (black circle) and MHP (blue triangle) at Backgarden from 19–30 July 2006 where vertical bars show the standard deviation.

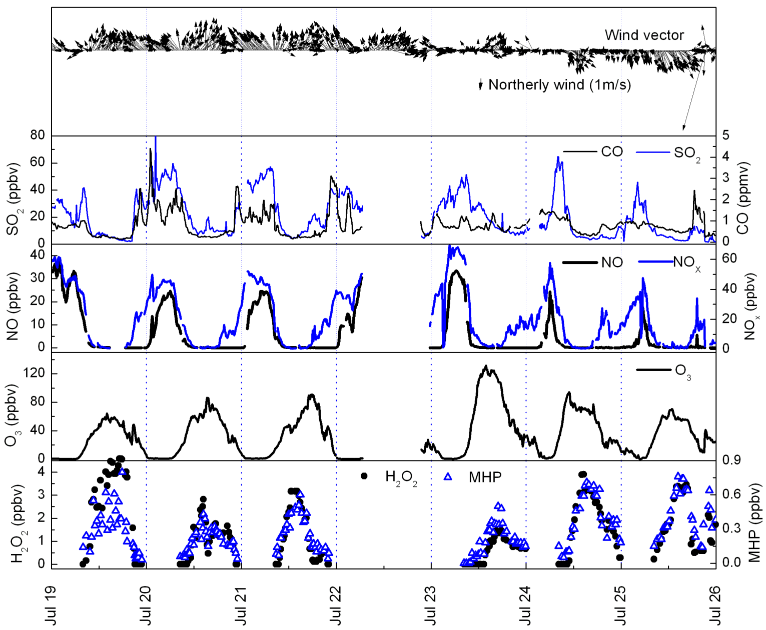

Fig. 4. Diurnal profile of wind speed, wind direction, NO, NO_x, SO_2, CO, O_3, and H_2O_2 and MHP measured at Backgarden on 19–25 July 2006.

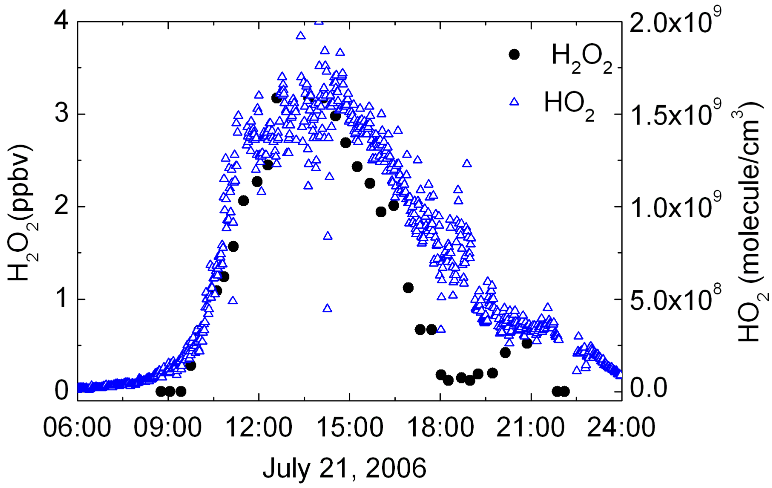

Fig. 5. Concentration profiles of HO_2 and H_2O_2 measured at Backgarden 21 July 2006.

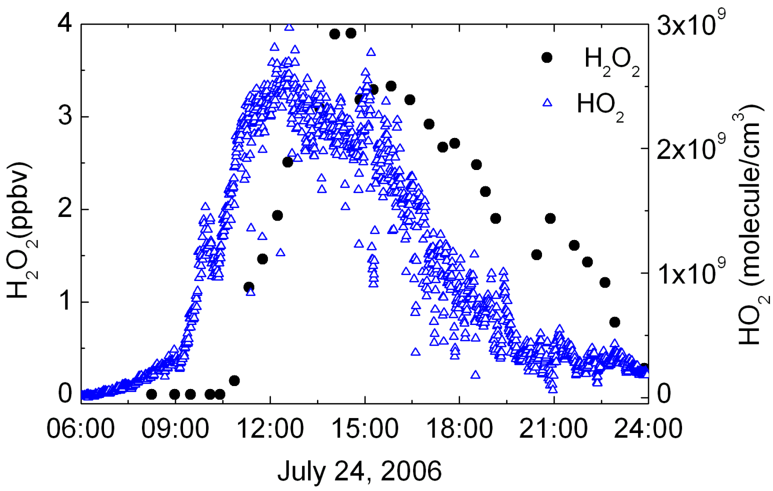

Fig. 6. Diurnal profiles of HO_2 and H_2O_2 measured at Backgarden on the 24 of July, 2006, showing a high level of H_2O_2 at night.

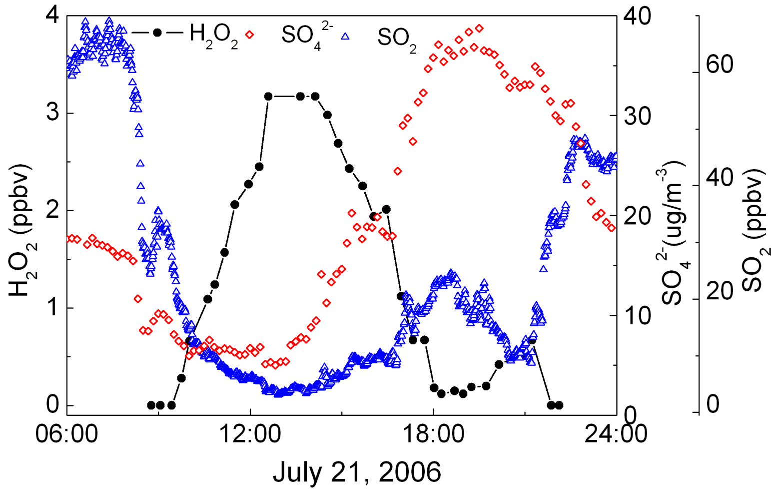

Fig. 7. Diurnal profiles of H_2O_2, sulfate and SO_2 on 21 July.

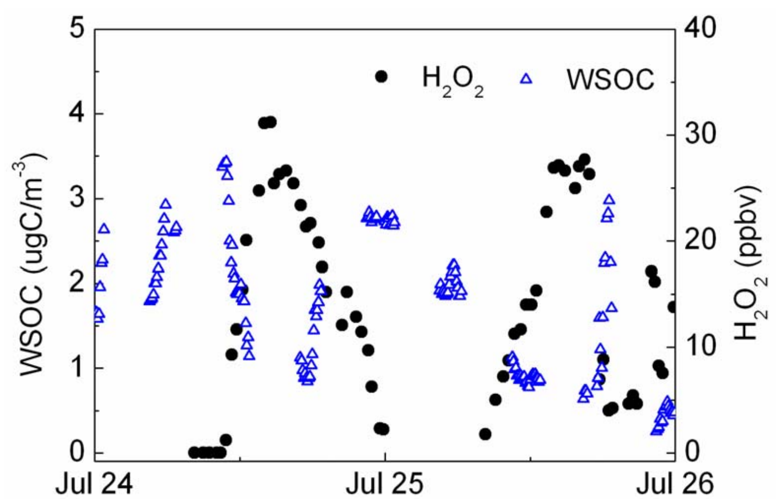

Fig. 8. Diurnal profiles of H_2O_2 and WSOC measured on 24 and 25 July.