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Methyl hydroperoxide (CH₃OOH) in urban, suburban and rural atmosphere: ambient concentration, budget, and contribution to the atmospheric oxidizing capacity

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Abstract. Methyl hydroperoxide (MHP), one of the most important organic peroxides in the atmosphere, contributes to the tropospheric oxidizing capacity either directly as an oxidant or indirectly as a free radical precursor. In this study we report measurements of MHP from seven field campaigns at urban, suburban and rural sites in China in winter 2007 and summer 2006/2007/2008. MHP was usually present in the order of several hundreds of pptv level, but the average mixing ratios have shown a wide range depending on the season and measuring site. Primary sources and sinks of MHP are investigated to understand the impact of meteorological and chemical parameters on the atmospheric MHP budget. The MHP/(MHP+H_2O_2) ratio is also presented here to examine different sensitivities of MHP and H_2O_2 to certain atmospheric processes. The diurnal cycle of MHP/(MHP+H_2O_2), which is out of phase with that of both H_2O_2 and MHP, could imply that MHP production is more sensitive to the ambient NO concentration, while H_2O_2 is more strongly influenced by the wet deposition and the subsequent aqueous chemistry. It is interesting to note that our observation at urban Beijing site in winter 2007 provides evidence for the occasional transport of MHP-containing air masses from the marine boundary layer to the continent. Furthermore, the contribution of MHP as an atmospheric oxidant to the oxidizing capacity of an air parcel is assessed based on the "Counter Species" concept.
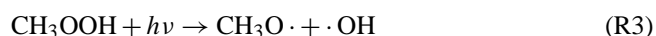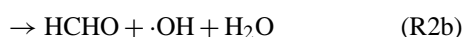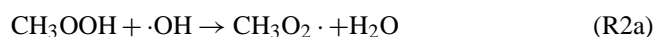
1 Introduction

Peroxides (hydrogen peroxide and organic peroxides) play an important role in atmospheric processes. They are not only among the principle oxidants in their own right, primarily as important oxidants of SO_2 in cloud or rain droplets (Penkett et al., 1979; Martin et al., 1981; Calvert et al., 1985), but also act as temporary reservoirs for important oxidizing radicals (Madronich and Calvert, 1990; Lightfoot et al., 1992). Furthermore, they are thought to have some toxic effects on plants (Hewitt et al., 1990; Polle and Junkermann, 1994a, b). As one of the main organic peroxides in the atmosphere, methyl hydroperoxide (MHP, CH₃OOH) has a longer lifetime and a lower solubility in water, compared to H_2O_2 (Cohan et al., 1999; Wang and Chen, 2006). It can be transported vertically and horizontally at a large scale, consequently leading to the redistribution of HO_x and RO_x radicals in different altitudes and different regions (Jaegle et al., 1997; Cohan et al., 1999; Mari et al., 2000; Ravetta et al., 2001). MHP also contributes to the formation of water-soluble organic compounds (WSOC) and atmospheric secondary sulfates (Claeys et al., 2004; Böge et al., 2006; Kroll et al., 2006; Hua et al., 2008).

The main source for MHP is the combination of HO_2 and CH_3O_2 radicals (Reaction R1a), which are produced through the oxidizing processes of CO, CH_4 as well as other alkanes and alkenes. The extent to which Reaction (R1a) proceeds depends upon solar radiation, temperature, and concentrations of O_3, CO, NO_x, and hydrocarbons.

$$CH_3O_2 \cdot + HO_2 \cdot \xrightarrow{0.6} CH_3OOH + O_2 \tag{R1a}$$

$$\xrightarrow{0.4} HCHO + H_2O + O_2 \tag{R1b}$$
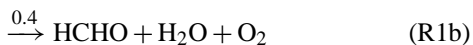
MHP has also been detected as a product from the ozonolysis of alkenes such as ethene, isoprene and α-pinene (Gäb et al., 1985; Hewitt and Kok, 1991; Horie et al., 1994; Gäb et al., 1995), and its yield in those reactions is not dependent on the presence of water vapor (Horie et al., 1994). In addition, biomass burning was also found as a potentially important source of MHP (Snow et al., 2007). Sinks of MHP are primarily photolysis, reaction with the hydroxy radical, and loss by physical deposition. The dry deposition velocity of MHP is 30 times smaller than that of H$_2$O$_2$ (Hauglustaine et al., 1994). Wet deposition does not represent an important sink for MHP because of its low solubility (Lind and Kok, 1994). In the atmosphere, MHP mainly undergoes photolysis and its reaction with OH (Reactions R2 and R3), leading to its atmospheric lifetime of 2–3 days (Wang and Chen, 2006).

$$CH_3OOH + \cdot OH \rightarrow CH_3O_2 \cdot + H_2O \tag{R2a}$$

$$\rightarrow HCHO + \cdot OH + H_2O \tag{R2b}$$

$$CH_3OOH + h\nu \rightarrow CH_3O \cdot + \cdot OH \tag{R3}$$

Over the past two decades, MHP was determined to be the most abundant organic peroxide in the atmosphere, with a maximum concentration approaching or even higher than that of H$_2$O$_2$ (Heikes et al., 1996; Lee et al., 1998; Weinstein-Lloyd et al., 1998; O'Sullivan et al., 1999; Weller et al., 2000; Grossmann et al., 2003; Valverde-Canossa et al., 2005; Hua et al., 2008; Frey et al., 2005; He et al., 2010; Klippel et al., 2011). However, the atmospheric behavior of MHP is still less understood than H$_2$O$_2$, in spite of its potential importance in determining the oxidative character of the atmosphere.

The primary aim of this study is fourfold: (i) to quantify the contribution of typical sources and sinks to the atmospheric MHP budget and their dependence on meteorology; (ii) to investigate the different sensitivities of H$_2$O$_2$ and MHP to certain atmospheric processes; (iii) to provide evidence for the transport of MHP-containing air masses from the marine boundary layer to the continent; and (iv) to understand the impact of MHP on the oxidizing capacity of an air parcel as a radical reservoir.

2 Experimental

2.1 Measurement sites

Atmospheric MHP concentrations were investigated at 4 sites in China, namely, Backgarden (BG) in Guangzhou city, Guangdong Province (23.548° N, 113.066° E), Peking University campus (PKU) in Beijing city (39.991° N, 116.304° E), Yufa site (YF) in suburban Beijing (39.514° N,

116.304° E), and Mazhuang site (MZ) in Tai'an city, Shandong Province (36.150° N, 116.133° E). The meteorological conditions and measured species for the 4 sites are shown in Table 1.

The BG site is a rural site located in the north of the central Pearl River Delta Region (PRD) and $\sim$ 60 km northwest of Guangzhou, the capital city of Guangdong Province. BG does not have significant local vehicle emission and can be treated as a regional background site. The sampling inlet was mounted on the roof of a three-story hotel building ($\sim$ 14 m above ground), which is located next to a 2.7 km^2 reservoir in a rural resort surrounded by a large area of farmland and forest. The MHP measurement was carried out during 12–31 July 2006 (BG-summer 2006).

The PKU site is located in the northern downtown of Beijing city, surrounded by several electronic supermarkets, institutes, campuses, residential apartments and two major streets at its east and south which are often congested. The sampling inlet was mounted on the roof of a six-story building ($\sim$ 26 m above the ground). The MHP measurement was carried out during 11–30 August 2006 (PKU-summer 2006), 16 January–5 February 2007 (PKU-winter 2007), 3–31 August 2007 (PKU-summer 2007), and 12 July–31 August 2008 (PKU-summer 2008).

The MZ site is a rural site located 40 km southwest of Tai'an, a middle city in Shandong province, northeast of China. The sampling inlet was mounted on the roof of a container ($\sim$ 5 m above the ground) on the playground of a primary school. It is surrounded by farmland, except for a national highway which passes by 1 km to the north. The MHP measurement was carried out during 29 June–31 July 2007 (MZ-summer 2007). More details about the BG, PKU and MZ sites can be found in our previous work (Hua et al., 2008; Zhang et al., 2010).

The YF site is a suburban site $\sim$ 65 km south of downtown Beijing. No significant local emissions are present in the vicinity of this site and the vegetation coverage in Yufa is $\sim$ 50 %. The sampling inlet was mounted on the roof of a four-story building ($\sim$ 16 m above the ground) in the campus of Huangpu University. MHP was measured on 1–12 September 2006 (YF-summer 2006), when the weather was characterized by sunshine with very low frequency of rain events.

2.2 Measurement method for MHP

A ground-based apparatus for measuring MHP was set up by using a scrubbing coil collector to sample ambient air, followed by in situ analysis by high-performance liquid chromatography (HPLC) coupled with post-column derivatization and fluorescence detection. Specifically, ambient air was drawn by a vacuum pump through a 6 m Teflon tube (1/4 inch O.D.) with a flow rate of 2.7 slm (standard liters per minute). The air samples were collected in a thermostatically controlled glass coil collector, at a temperature of

Table 1. Meteorological and chemical parameters for the seven measurements.

Site	T (°C)	Wind		RH (%)	P (hPa)	Species measured
		Speed (m s^{-1})	Prevailing direction			
BG-summer 06	29.5 ± 3.4	1.9 ± 1.2	southerly southeasterly	76.2 ± 14.4	1001 ± 4	NO$_x$, O$_3$, SO$_2$, CO, PAN, NMHCs, PO, HO$_x$, RO$_x$
PKU-summer 06	26.1 ± 4.6	1.6 ± 1.4	southerly westerly	65.1 ± 20.1	1002 ± 5	NO$_x$, O$_3$, SO$_2$, CO, PAN, NMHCs, PO, RO$_x$
PKU-summer 07	29.3 ± 4.3	1.5 ± 0.8	southerly easterly	54.0 ± 15.3	1001 ± 6	NO$_x$, O$_3$, SO$_2$, CO, PAN, NMHCs, PO, RO$_x$
PKU-summer 08	28.1 ± 5.6	1.0 ± 0.9	southerly	67.0 ± 18.5	998 ± 4	NO$_x$, O$_3$, SO$_2$, CO, PAN, NMHCs, PO
PKU-winter 07	1.7 ± 6.6	1.7 ± 1.0	westerly northerly	38.6 ± 11.5	1020 ± 3	NO$_x$, O$_3$, SO$_2$, CO, NMHCs, PO
YF-summer 06	21.2 ± 9.1	2.2 ± 1.8	southerly southeasterly	62.8 ± 32.1	1007 ± 11	NO$_x$, O$_3$, SO$_2$, CO, PAN, NMHCs, PO, HO$_x$, RO$_x$
MZ-summer 07	28.7 ± 5.8	1.2 ± 1.3	southerly southeasterly	70.4 ± 19.6	1001 ± 5	NO$_x$, O$_3$, SO$_2$, CO, NMHCs, PO

Note: PAN, peroxyacetyl nitrate; PO, peroxides.

10 °C for BG-summer 2006 and 4 °C for other observations. The stripping solution, acidified 18 MΩ water (H$_3$PO$_4$, pH 3.5) was delivered into the collector by a pump at a rate of 0.2 ml min^{-1}. The collection efficiency has been determined as ∼ 85 % for MHP and ∼ 100 % for H$_2$O$_2$ at a temperature of 10 °C in our previous study (Hua et al., 2008). After the sampled air passed through the coil collector, the stripping solution was removed from the separator using a peristaltic pump and immediately injected into the HPLC valve, from which 100 μl was analyzed by HPLC 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 of Hemin. This method has been applied to measure the ambient H$_2$O$_2$, MHP, and peroxyacetic acid (PAA), with the detection limit as 9 pptv, 20 pptv, and 12 pptv, respectively. For the observations in PKU-summer 2006 (21–30 August), YF-summer 2006, PKU-summer 2007/2008, PKU-winter 2007, and MZ-summer 2007, the air samples collected by the scrubbing coil were automatically injected into the HPLC continuously at an interval of 24 min. But in the BG-summer 2006 and PKU-summer 2006 (11–20 August), the sample analysis was performed in a quasi-continuous mode with an interval of 20–60 min. Only few samples were measured at night and in the early morning. More details on the instrument setup and methods for the peroxides measurement can be found in our previous work (Xu and Chen, 2005; Hua et al., 2008; Zhang et al., 2010).

2.3 Measurement method for free radicals

HO$_2$ radicals were measured by a laser-induced fluorescence instrument, operated by Forschungszentrum Jülich (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 accuracy of measurements is estimated to be ±20 %. Details can be found in Holland et al. (2003). RO$_x$ (RO$_2$ + HO$_2$) radicals were measured by chemical amplification (PERCA), operated by Peking University. Basically, RO$_x$ are measured via amplification of NO$_2$ by RO$_x$ in the presence of NO and CO through a chain reaction. The amount of amplified NO$_2$ is determined by a NO$_2$-luminal chemiluminescence detector. The detection limit was 1–5 pptv and the systematic uncertainty was estimated to be ±60 %. Details can be found in Li (2009).

2.4 Modeling methodology

A 0-D box model with the Carbon Bond Mechanism-Version IV (CBM-IV) developed by Gery et al. (1989) and updated by Adelman (1999) was performed to simulate the importance of MHP as a reservoir of free radicals in the oxiding capacity in an air parcel. The CBM-IV mechanism includes 106 photochemical reactions concerning 40 species. The box model assumed a well-mixed atmosphere to simplify the treatment of diffusion and transportation and to represent chemical mechanisms in great detail. Meteorological

Table 2. Statistical distribution of atmospheric MHP mixing ratios (ppbv) for the seven measurements.

	Mean	Min	Max	Median	5 %	25 %	75 %	95 %
PKU-summer 2006	0.17	0.01	1.10	0.14	0.01	0.08	0.21	0.44
PKU-summer 2007	0.19	0.01	0.90	0.17	0.01	0.09	0.26	0.44
PKU-winter 2007	0.30	0.01	2.40	0.21	0.01	0.01	0.44	1.01
PKU-summer 2008	0.16	0.01	0.19	0.09	0.01	0.01	0.25	0.54
BG-summer 2006	0.26	0.01	0.76	0.24	0.07	0.16	0.33	0.58
YF-summer 2006	0.10	0.01	0.47	0.08	0.01	0.04	0.13	0.28
MZ-summer 2007	0.18	0.01	0.78	0.15	0.01	0.06	0.28	0.44

parameters, i.e. radiation intensity, temperature, relative humidity, and mixing layer height were from 10 min average observational data during BG-summer 2006. The initial CO, SO$_2$, NO$_x$, CH$_4$, and NMHCs concentrations input were 0.60 ppm, 5.01 ppb, 24.20 ppb, 1.85 ppm, and 4.42 ppb, respectively. There are additional emissions of 1.2 ml m^{-2} anthropogenic VOCs, 1.2 ml m^{-2} biogenic VOCs, 0.24 ml m^{-2} NO$_x$, 0.20 ml m^{-2} SO$_2$, respectively, every one minute. The simulation was carried out on a 24-h basis and we chose the period after 72 h for analysis.

3 Results and discussion

3.1 Ambient concentrations

Figure 1 shows 10 days of continuous MHP, together with H$_2$O$_2$ measurements for each campaign. MHP was usually present with a level of hundreds of pptv during the seven observations. The MHP mixing ratios in BG-summer 2006, PKU-summer 2006/2007/2008, and MZ-summer 2007 were generally at the same level, while in YF-summer 2006, the mixing ratio was lower. In PKU-winter 2007, MHP was often below the detection limit, with a few high concentration episodes. A statistical distribution of MHP is shown in Table 2 and Fig. 2a. There is no big difference in MHP average mixing ratios between urban and suburban. A clear diurnal cycle was evident in BG-summer 2006, PKU-summer 2006/2007/2008, and MZ-summer 2007, but less distinct in YF-summer 2006 and PKU-winter 2007.

3.2 MHP/(MHP+H$_2$O$_2$) ratio

The MHP/(MHP+H$_2$O$_2$) ratios of the seven observations are shown in Fig. 2b. Note that concentrations below the detection limit were treated as the corresponding detection limit. In PKU-winter 2007, the concentrations of both H$_2$O$_2$ and MHP were often below the detection limit. Since the detection limit for MHP is higher than for H$_2$O$_2$, the calculated MHP/(MHP+H$_2$O$_2$) ratio in PKU-winter 2007 is higher than the other six observations, which were in good agreement with previous observations, ranging from 0.20 to 0.57 (Weller and Schrems, 1993; Slemr and Termmel, 1994; Weller et al., 2000; Riedel et al., 2000). The aver-

age MHP/(MHP+H$_2$O$_2$) ratio in PKU-summer 2006 was much lower than those in PKU-summer 2007 and 2008 because we did not have the night measurement for about half of the time in PKU-summer 2006. A typical diurnal variation of MHP/(MHP+H$_2$O$_2$) ratio in PKU-summer 2008 is shown in Fig. 3, together with corresponding H$_2$O$_2$ and MHP mixing ratios. The diurnal profile of MHP is consistent with that of H$_2$O$_2$ during daytime, which can be explained by vertical mixing and local photochemical production in a sunlit day. From sunrise, the photochemical production initiated and MHP concentration started to rise, reaching a maximum level at 14:00 LT. Its level remained relatively high in the late afternoon and sometimes a shoulder peak was observed around 17:00 LT, which can be attributed to the secondary emission of pollutants during traffic hours. The MHP/(MHP+H$_2$O$_2$) ratio, however, was out phase with H$_2$O$_2$ and MHP mixing ratios, peaking during the night and early morning ($\sim$ 00:00–06:00) and decaying rapidly in the afternoon ($\sim$ 15:00–19:00). The high values in the night and early morning indicate a preferential depletion of H$_2$O$_2$ to MHP. The shallow boundary layer height accelerates the dry deposition processes in particular for H$_2$O$_2$ during night, resulting in a substantial decease in H$_2$O$_2$ concentration. In addition, the high relative humidity (RH) during nighttime accelerates two H$_2$O$_2$ removal pathways: deposition to water droplets and aqueous-phase oxidation of S(IV), both of which are much less important for MHP.

It is known that the presence of NO could suppress the formation of peroxides by reaction with HO$_2$ and RO$_2$ radicals. Frey et al. (2005) suggested through a box model calculation that MHP production is more sensitive to the variation of NO concentration, because the reaction of NO with HO$_2$ forms OH, which may simply be recycled to HO$_2$ and is again available for peroxide formation. But in the case of CH$_3$O$_2$, HCHO is yielded, and MHP cannot be produced from the subsequent reactions. Moreover, the calculated OH increased with increasing NO. Since the reaction of MHP with OH is more rapid than that for H$_2$O$_2$, the decrease of MHP tends to be more pronounced with increasing NO. Our measurements provide evidence for the different sensitivities of MHP and H$_2$O$_2$ to NO variations. In PKU-summer 2008, the average MHP/(MHP+H$_2$O$_2$) ratio was higher than that
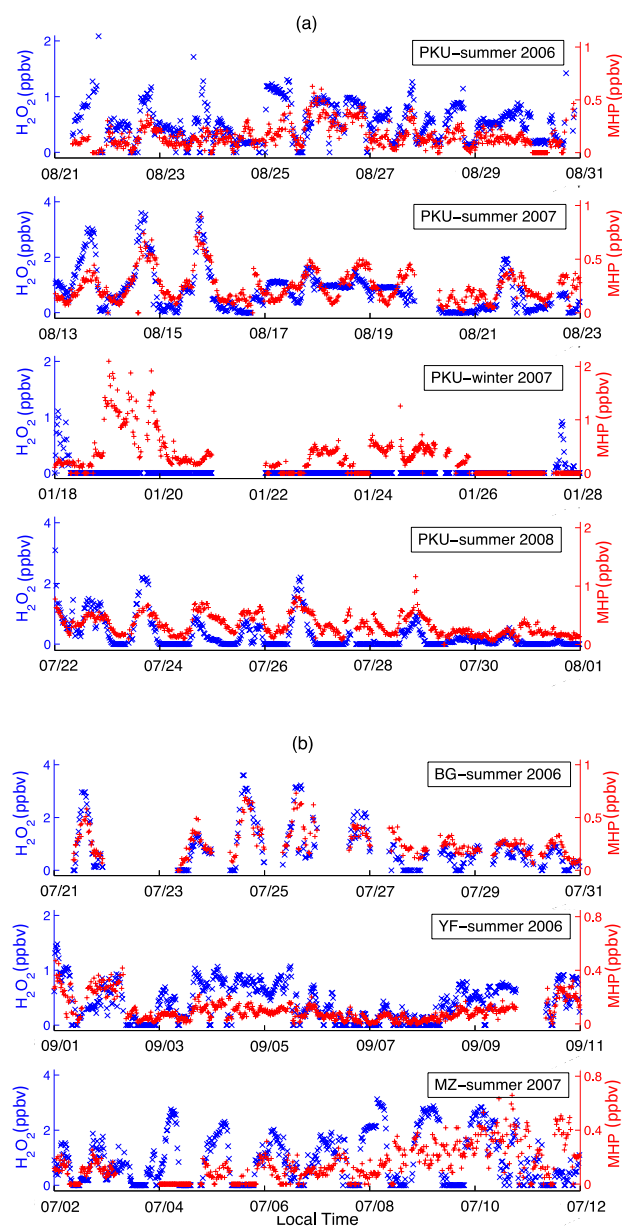
Fig. 1. Temporal profiles of atmospheric MHP and H$_2$O$_2$ during seven observations. **(a)** Urban sites and **(b)** suburban and rural sites.
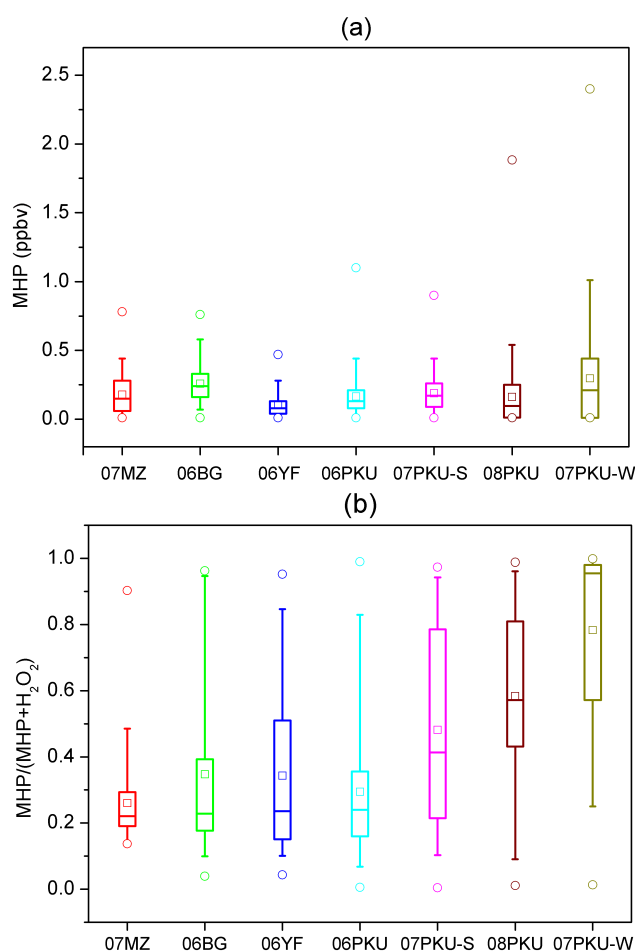

Fig. 2. MHP distribution **(a)** and MHP/(MHP+H$_2$O$_2$) ratio **(b)** during the seven observations: MZ-summer 2007 (07MZ), June 30–July 31; BG-summer 2006 (06BG), 18–30 July; YF-summer 2006 (06YF), 1–12 September; PKU-summer 2006 (06PKU), 11–30 August; PKU-summer 2007 (07PKU-S), 3–30 August; PKU-summer 2008 (08PKU), 13 July–30 August; and PKU-winter 2007 (07PKU-W), 16 January–5 February. Each box has dashes for the lower quartile, median, and upper quartile values. The squares in the boxes are the mean values. The whiskers range from the 5 % to 95 % of the total samples. The circles are the minima and maxima.

in PKU-summer 2006 and 2007, although the three measurements were performed at the same time of year nominally August. The primary difference is that a full scale control of atmospheric pollutants was implemented to improve the air quality prior to the 2008 Beijing Olympic Games, resulting in a significant decrease in the emission of pollutants, such as NO$_x$, CO, and SO$_2$, in urban Beijing (Wang et al., 2009). This suggests a transition from a H$_2$O$_2$ dominated regime to an organic peroxide dominated regime with decreasing NO$_x$. Note that the dependency of the MHP/(MHP+H$_2$O$_2$) on the NO$_x$ level change might be overestimated here because of the interference of CO reduction, which leads to a decrease

in HO$_2$ radical concentration. Assuming the level of methane remains constant, reductions in CO will result in strong decrease in the primary production of H$_2$O$_2$, whereas MHP will be affected only marginally. In view of this effect, we also presented here three daily basis measurements, see Fig. 4, which were carried out on 24 August 2006, 15 August 2007 and 23 July 2008, respectively. The CO concentrations, together with the meteorology conditions were consistent for the last two measurements, whereas the NO concentration in the morning of 15 August 2007 was substantially higher than 23 July 2008. As a result, the MHP/(H$_2$O$_2$+MHP) ratio was much lower in the presence of high level of NO$_x$. It is also interesting to note that a SO$_2$ pollution episode arrived
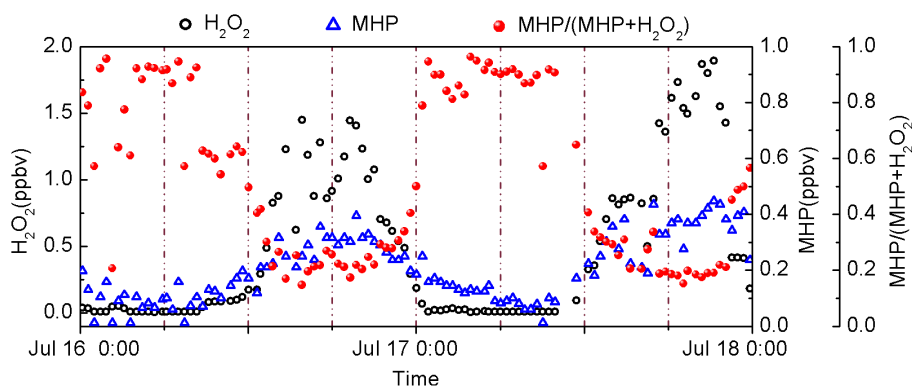
Fig. 3. MHP/(MHP+H$_2$O$_2$) ratio, together with concentrations of MHP and H$_2$O$_2$ in PKU-summer 2008.
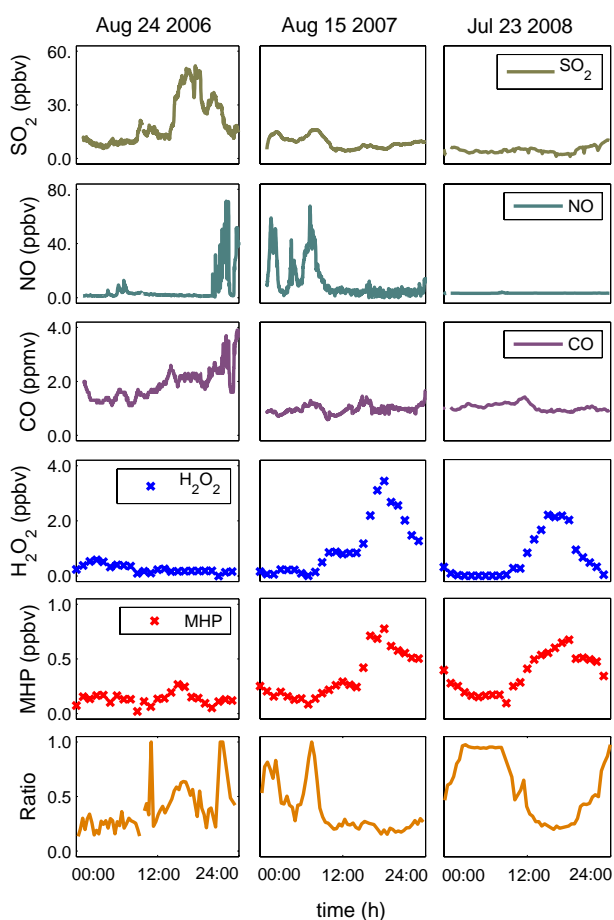

Fig. 4. The dependency of MHP/(MHP+H$_2$O$_2$) ratio to NO level change. SO$_2$ and CO levels are shown as a comparision.

at 14:00 LT in the afternoon of 24 August 2006. As a result, the MHP/(H$_2$O$_2$+MHP) ratio started to increase, suggesting a preferential depletion of H$_2$O$_2$ to MHP via the aqueous phase oxidation of SO$_2$. Considering the different roles of MHP and H$_2$O$_2$ in the atmospheric radicals distribution and

the formation of secondary sulfates, the transition between H$_2$O$_2$ and MHP dominating regime might have potential impacts on the atmospheric chemistry.

3.3 MHP budget

We present here two cases, namely, Case 1, which was investigated during 09:30–12:30 on 21 July in BG-summer 2006 and Case 2, which was investigated during 13:20–14:40 on 7 September in YF-summer 2006, to study the contribution of different sources and sinks to the atmospheric MHP budget. Case 1 was a sunny day and the average meteorological parameters (arithmetic mean ± standard deviation) were: $32.3 \pm 2.4\,°C$ ambient temperature, $57.5 \pm 9.3\,\%$ ambient relative humidity, 1001.4 ± 0.7 hPa ambient pressure, and $1.5 \pm 0.9\,\mathrm{m\,s^{-1}}$ local wind speed. Case 2 was a cloudy day and the average meteorological parameters (arithmetic mean ± standard deviation) were: $25.7 \pm 0.9\,°C$ ambient temperature, $55.2 \pm 9.2\,\%$ ambient relative humidity, 1006.1 ± 0.7 hPa ambient pressure, and $1.6 \pm 1.7\,\mathrm{m\,s^{-1}}$ local wind speed. The MHP formation via the combination of HO$_2$ and CH$_3$O$_2$ radicals was investigated based on the observed free radical mixing ratios. Figure 5 shows the time-dependent MHP mixing ratios, together with RO$_x$ and HO$_2$ radical concentrations. Photochemical simulations with Regional Atmospheric Chemistry Mechanism (RACM) have shown that CH$_3$O$_2$ radicals account for 17 % and 15 % of the total RO$_x$ radicals during noontime for these two cases, respectively (Li et al., 2009). The average production rates of MHP from the reaction of CH$_3$O$_2$ with HO$_2$ for Case 1 and Case 2 can be calculated as 0.39 and 0.077 ppbv h^{-1}, respectively. The photochemical production of ambient MHP varies significantly for the two cases, depending strongly on the solar radiation. The ozonolysis of alkenes has been reported to produce peroxides including MHP, although the detailed mechanism for the formation of MHP is still in debate. Assuming a 5 % MHP yield (Hewitt and Kok, 1991; Horie et al., 1994; Gäb et al., 1995) from the ozonolysis of 12 dominating alkenes shown in Table 3, the average

Table 3. Reaction rates of 12 C$_2$–C$_5$ alkenes with O$_3$ for Case 1 (09:30–12:30 on 21 July 2006 at BG site) and Case 2 (13:20–14:40 on 7 September 2006 at YF site).

Alkenes	Rate coefficient $\times 10^{-18}$ cm^3 molecule^{-1} s^{-1}	Reference	Concentration (ppbv)		Rate (ppbv h^{-1})	
			Case 1	Case 2	Case 1	Case 2
Ethene	1.7	Atkinson et al. (1999)	3.41	3.43	0.0200	0.038
Propene	10.6		1.00	0.61	0.0360	0.042
trans-2-Butene	10.0	Estimated in this work	0.01	0.01	0.0004	0.001
1-Butene	10.2	Avzianova and Ariya (2002)	0.06	0.04	0.0020	0.003
iso-Butene	11.1	Wegener et al. (2007)	0.52	0.22	0.0200	0.016
cis-2-Butene	129.0		0.01	0.01	0.0060	0.008
1,3-Butadiene	6.2	Treacy et al. (1992)	0.01	0.06	0.0030	0.002
trans-2-Pentene	10.0	Estimated in this work	0.00	0.01	0.0000	0.001
cis-2-Pentene	10.0		0.00	0.01	0.0000	0.001
Isoprene	13.4	Khamaganov and Hites (2001)	0.84	0.58	0.0380	0.050
1-Pentene	10.0	Avzianova and Ariya (2002)	0.01	0.05	0.0003	0.003
3-Methylbutene	14.2	Grosjean and Grosjean (1996)	0.01	0.01	0.0004	0.001
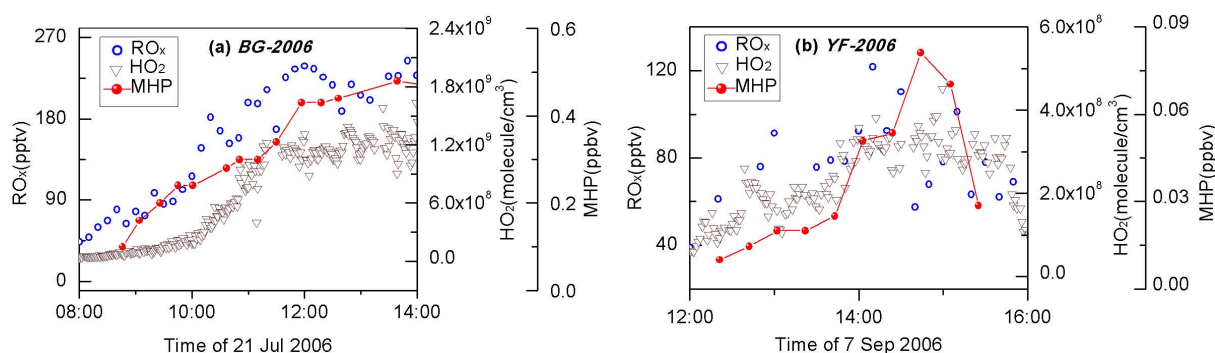
Fig. 5. Profiles of HO$_2$, RO$_x$ (OH, HO$_2$, RO, and RO$_2$) and MHP concentrations measured at BG site on 21 July 2006 and at YF site on 9 September 2006.

MHP production rates from the ozonolysis of these alkenes for the two cases were 0.0063 and 0.0083 ppbv h^{-1}, respectively. It can be seen that the ozonolysis of alkenes accounts for up to ten percent of the total sources of MHP under weak photochemical activities. The dominant pathways for the removal of MHP in the troposphere include reaction with OH radicals (Reaction R2), photolysis (Reaction R3), and deposition. The photodecomposition parameters of MHP (absorption cross sections and quantum yields) were obtained from Sander et al. (2011). The deposition rate coefficient of MHP was estimated to be 0.8×10^{-5} s^{-1} according to Weller et al. (2000). For Case 1, the MHP loss rates through OH-reaction, photolysis and deposition were 0.065, 0.0050, and 0.0086 ppbv h^{-1}, respectively. For Case 2, the MHP loss rates were 0.0023 ppbv h^{-1} by OH-reaction, 0.00026 ppbv h^{-1} by photolysis, and 0.0012 ppbv h^{-1} by deposition.

Balancing the MHP production and removal pathways, from above gives a net increase of ~ 0.32 and ~ 0.081 ppbv h^{-1} for Case 1 and Case 2, respectively.

However the observed increase rates of MHP were lower, at ~ 0.11 and ~ 0.061 ppbv h^{-1}, respectively. To understand this overestimation, consider that the reaction between CH$_3$O$_2$ and HO$_2$ does not yield 100 % MHP (Reaction R1a), but undergoes another channel to yield either HCHO (Reaction R1b). The branching ratio for Reaction (R1a) has been under debate, with estimations ranging from 60 % (Jenkin et al., 1988) to almost 100 % (Wallington, 1991; Lightfoot et al., 1992; Wallington et al., 1992). In this calculation, a ~ 60 % MHP yield leads to a better agreement with the observational values, see Fig. 6. In many atmospheric models, the reaction between CH$_3$O$_2$ and HO$_2$ is assumed to proceed exclusively by Reaction (R1a) (Weller et al., 2000; Elrod et al., 2001), which could cause the overestimation of MHP but underestimation of HCHO. Since MHP and HCHO are characterized by quite different photochemical activities, this uncertainty on MHP and HCHO simulation will further impact the HO$_x$ cycling and O$_3$ production efficiency.
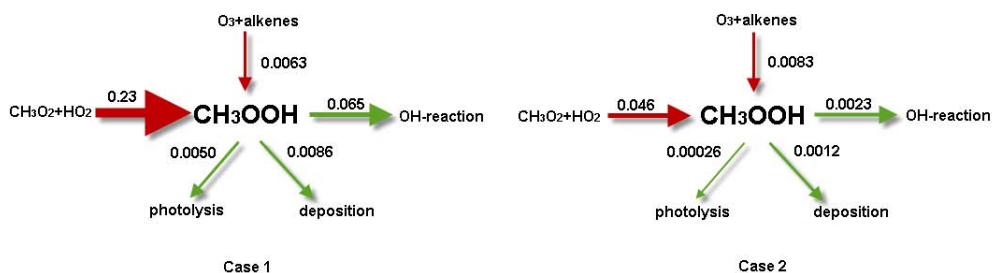
Fig. 6. Calculated sources and sinks of MHP (ppbv h^{-1}) for Case 1 (09:30–12:30 on 21 July in BG-summer 2006) and Case 2 (13:20–14:40 on 7 September 2006 in YF-summer 2006).
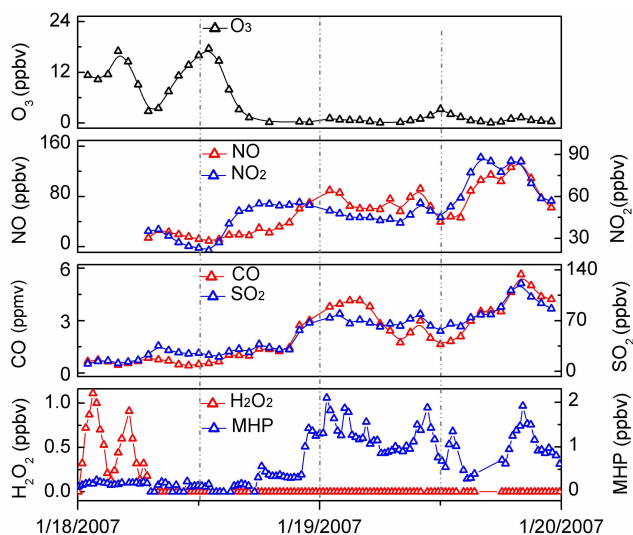

Fig. 7. Profiles of H$_2$O$_2$, MHP, CO, SO$_2$, NO, NO$_2$ and O$_3$ concentrations at PKU site on 18 January and 19 January 2007.

3.4 MHP in winter: a case study for regional transport

It is known that MHP levels are higher in summer than winter, which agrees with enhanced photochemical production due to stronger solar radiation. However, MHP in PKU-winter 2007 was often detected at a significant level, sometimes even higher than summer. As shown in Fig. 7, MHP on 19 January maintained a high level (0.3–2.1 ppbv) during most of the day, with no typical diurnal variation. The high concentration of MHP cannot result from photochemical production because NO was extremely high ($\sim$ 120 ppbv) at the same time, which would substantially consume HO$_2$ and CH$_3$O$_2$ and as a result suppress the formation of MHP. The second MHP formation pathway, ozonolysis of alkenes, was unlikely to contribute to the high MHP level, given the very low O$_3$ concentration. It is interesting to note that MHP showed a positive correlation with primary pollutants such as CO, SO$_2$ and NO on 19 January, which may imply a regional transport of air mass. Considering that the atmospheric lifetime of MHP is $\sim$ 2–3 days (Wang and Chen,
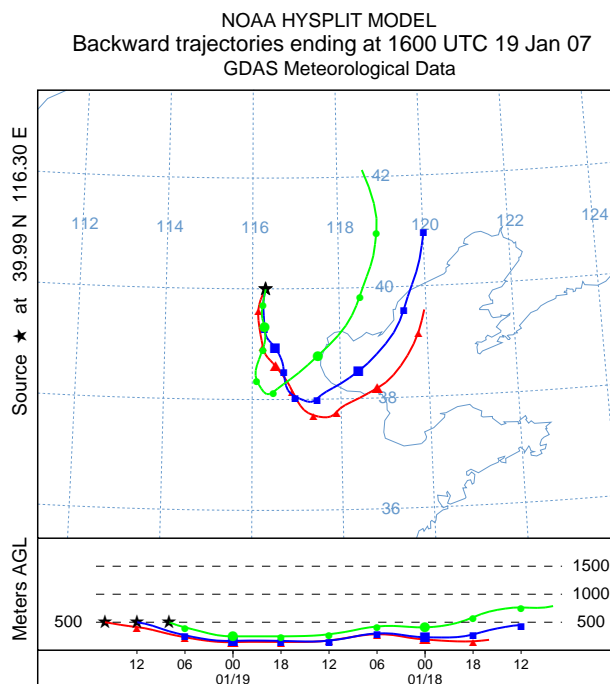

Fig. 8. 48-h-back trajectories reaching PKU site at 00:00, 20 January (red line), 20:00, 19 January (blue line), and 16:00, 19 January 2007 (green line), Beijing local time (UTC+8 h).

2006), a 48-h-back trajectory reaching PKU site PKU site at 00:00, 20 January (red line), 20:00, 19 January (blue line), and 16:00, 19 January 2007 (green line), obtained from NOAA (www.arl.noaa.gov) is shown in Fig. 8. The air mass reaching PKU site at 20:00, 19 January and 00:00, 20 January was originated from or by way of the Bohai Sea, locating in the Western Pacific Ocean, and the concentration of MHP was elevated at that time. The air mass reaching PKU site at 16:00 19 January originated from the continent, and did not result in an increase in MHP level. To the best of our knowledge, there is no report for the direct emission of MHP from the ocean. However, the emission of CH$_4$ from coastal and marine areas has been observed widely (Heyer and Berger, 2000; Rehder et al., 2002; Amouroux et al., 2002; Schmale et al., 2005; Chen and Tseng, 2006), and CH$_3$I is considered
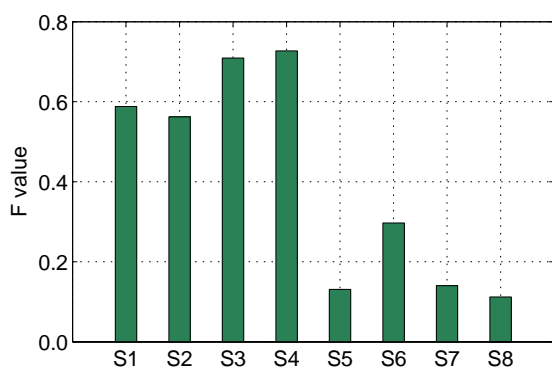
Fig. 9. F-values of eight important oxidants in an air parcel after 72 h simulation. These eight oxidants are OH radical (S1), $HO_2\cdot$ radical (S2), $CH_3OO\cdot$ radical (S3), $CH_3CH_2OO\cdot$ radical (S4), $CH_3C(O)OO\cdot$ radical (S5), HCHO (S6), H_2O_2 (S7), and MHP (S8).

as a unique emission from the ocean (Yokouchi et al., 2001; Li et al., 2001; Bell et al., 2002). Both CH_4 and CH_3I could produce CH_3O_2 and then MHP by photochemical reactions (Enami et al., 2009). So a certain level of MHP is expected in the marine boundary layer, which has been confirmed by previous observations (Weller et al., 2000; Riedel et al., 2000; Klippel et al., 2011). Our measurement provides evidence for the high level of MHP that originates from the marine boundary layer and transports to the continent. Since MHP is an important component of the atmospheric oxidants and a reservoir for the HO_x family, this transport may contribute to the redistribution of the atmospheric oxidant and HO_x radicals between the ocean and land.
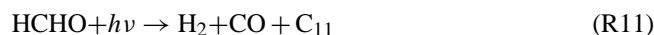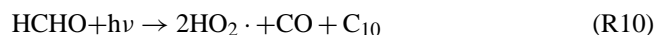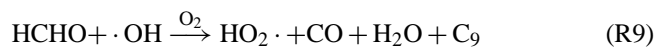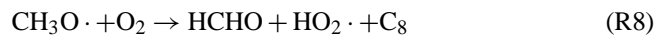
3.5 Contribution of MHP to the atmospheric oxidizing capacity

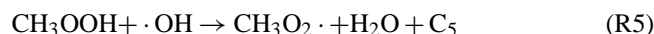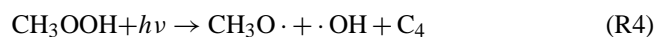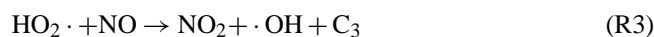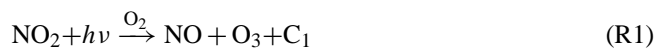The oxidizing capacity (oxidation power) of an air parcel is defined as the rate at which OH is produced (Lelieveld, et al., 2002, 2004). MHP is an important reservoir for peroxy radicals and the photolysis of MHP could release OH radicals. MHP is involved in the radical balance as both a source and sink, so that the variation in MHP levels would affect the OH production and thus, the oxidizing capacity in the atmosphere. The relative importance of MHP in the oxidizing capacity of an air parcel is examined based on the "Counter Species" concept proposed by Leone and Seinfeld (1984). Counter species are fictitious products (mathematical quantities) added to the reactions in a complex mechanism that allow one to determine the relative contributions of individual reactions to the overall behavior of the mechanism. Since they are produced only in one reaction and are not consumed, they can count the number of times for a specific reaction that occurred until any time t. We added 67 counter species (C_1–C_{67}) in the CBM-IV mechanism to track the flows of several important oxidants in the atmosphere. Many species in the atmosphere can produce peroxy radicals that can ox-

idize NO to NO_2, causing the ultimate accumulation of O_3 and consequently OH radicals, which is the indicator of oxidizing capacity. We use the ability of converting NO to NO_2 as a standard to evaluate the contribution of individual oxidants to the oxidizing capacity of an air parcel. Leone and Seinfeld (1984) defined "F_S" to determine the fraction of the molecules of any product species S that has led to NO to NO_2 conversions up until any time t:

$$F_S = \frac{\text{number of NO/NO}_2 \text{ conversions due to produced species S, up to time } t}{\text{number of moloucles S formed, up to time } t} \quad (1)$$

Let us consider the MHP chemistry in an air parcel as an example. Reactions involving the formation and removal of MHP include:

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 + C_1 \quad (R1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 + C_2 \quad (R2)$$

$$HO_2\cdot + NO \rightarrow NO_2 + \cdot OH + C_3 \quad (R3)$$

$$CH_3OOH + h\nu \rightarrow CH_3O\cdot + \cdot OH + C_4 \quad (R4)$$

$$CH_3OOH + \cdot OH \rightarrow CH_3O_2\cdot + H_2O + C_5 \quad (R5)$$

$$CH_3O_2\cdot + NO \rightarrow CH_3O\cdot + NO_2 + C_6 \quad (R6)$$

$$CH_3O_2\cdot + HO_2\cdot \rightarrow CH_3OOH + O_2 + C_7 \quad (R7)$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot + C_8 \quad (R8)$$

$$HCHO + \cdot OH \xrightarrow{O_2} HO_2\cdot + CO + H_2O + C_9 \quad (R9)$$

$$HCHO + h\nu \rightarrow 2HO_2\cdot + CO + C_{10} \quad (R10)$$

$$HCHO + h\nu \rightarrow H_2 + CO + C_{11} \quad (R11)$$

$$NO_2 + \cdot OH \rightarrow HNO_3 + C_{12} \quad (R12)$$
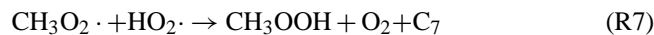
The conversion of NO to NO_2 occurs via Reactions (R2), (R3), and (R6). $HO_2\cdot$ radicals are produced via Reactions (R8), (R9), and (R10). So the F_S value for $HO_2\cdot$ radicals can be expressed as:

$$F_{HO_2} = \frac{C_3}{C_8 + C_9 + 2C_{10}} \quad (2)$$

Formaldehyde cannot oxidize NO to NO_2 directly, but the photolysis and OH oxidation of formaldehyde can produce $HO_2\cdot$ radicals. So the F_S value for formaldehyde can be expressed as:

$$F_{HCHO} = \frac{F_{HO_2}(C_9 + 2C_{10})}{C_8} \quad (3)$$

Using the definition and the method shown above, the F_S values of several important oxidants after 72 h simulation are shown in Fig. 9. We can see that a majority of the NO oxidations are caused by free radicals and that most of the remaining NO to NO_2 conversion is due to HCHO. The percent of NO to NO_2 conversion due to H_2O_2 chemistry is about the same as the percent conversion due to MHP chemistry. The contribution of MHP to the NO/NO_2 conversion is $\sim 1/4$ that of HO_2.

4 Conclusions

Atmospheric MHP concentrations at urban, suburban and rural sites of China were measured during 7 observations. MHP was usually present at hundreds of pptv level, with the average concentrations ranging from 0.10 ± 0.08 ppbv to 0.28 ± 0.32 ppbv. MHP shows a clear diurnal variation during sunny days in summer. The contributions of primary sources and sinks to the atmospheric MHP level under different weather conditions are investigated. Two conclusions can be drawn from the investigation of the MHP/(MHP+H$_2$O$_2$) ratio: (i) the diurnal variation of the MHP/(MHP+H$_2$O$_2$) ratio is out phase of the temporal profiles of H$_2$O$_2$ and MHP, indicating a preferential depletion of H$_2$O$_2$ to MHP during the night and early morning; and (ii) the elevated MHP/(MHP+H$_2$O$_2$) ratios in PKU-summer 2008, when mitigation of atmospheric pollution was implemented in Beijing, suggests that MHP is more sensitive to NO than H$_2$O$_2$. MHP that originated from the marine boundary layer and transported to land was observed in PKU-winter 2007, which implies the MHP production in the oceanic air might be an important source for the global average MHP. The importance of MHP as an atmospheric oxidant was evaluated using the "Counter Species" concept. The oxidizing capacity of MHP in an air parcel is $\sim$ 4–5 times lower than free radicals such as OH, HO$_2$, and RO$_2$, but at the same level as HCHO and H$_2$O$_2$. Note that the photochemical box model simulated a typical urban atmosphere in this study. Apparently, the impact of MHP on the free radical cycle should be more significant under low NO$_x$ environment, where RO$_2$+ HO$_2$ instead of RO$_2$+ NO chemistry dominates. We suggest that the study for MHP kinetics constitutes important tasks in gaining insight into the free radical chemistry and the oxidizing capacity of the atmosphere.

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