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Methyl hydroperoxide (CH_3OOH) 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 the diurnal cycle 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. Highly constrained box model is performed to study the influence of MHP on the free radical cycle. The simulation shows that MHP has a significant impact on the CH_3O_2 racial budget in the atmosphere. Furthermore, the contribution of MHP as an atmospheric oxidant to the overall tropospheric oxidizing capacity is also 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 subjected to S(IV) oxidation 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 et al., 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, CH_3OOH) 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 secondary organic aerosols (SOA) 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 1a), which are produced through the oxidizing processes of CO, CH_4 as well as other alkanes and alkenes. The extent to which Reaction (1a) proceeds depends upon solar radiation, temperature, and concentrations of O_3, CO, NO_x, and hydrocarbons.

$$CH_3O_2^{\cdot} + HO_2^{\cdot} \rightarrow CH_3OOH + O_2 \tag{1a}$$

$$\rightarrow HCHO + H_2O + O_2 \tag{1b}$$

$$\rightarrow CH_3OH + O_3 \tag{1c}$$

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_2O_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 2 and 3), leading to its atmospheric lifetime of 2–3 days (Wang and Chen, 2006).

$$CH_3OOH + {}^{\cdot}OH \rightarrow CH_3O_2^{\cdot} + H_2O \tag{2a}$$

$$\rightarrow HCHO + {}^{\cdot}OH + H_2O \tag{2b}$$

$$CH_3OOH + h\nu \rightarrow CH_3O^{\cdot} + {}^{\cdot}OH \tag{3}$$

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_2O_2 (Heikes et al., 1996; Lee et al., 1998; Weinstein-Lloyd et al., 1998; O'Sullivan et al., 1999; Wellet et al., 2000; Grossmann et al., 2003; Valverde-Canossa et al., 2005; Hua et al., 2008; Frey et al., 2009; He et al., 2010; Klippel et al., 2011). However, the atmospheric behavior of MHP is still less understood than H_2O_2, in spite of its potential importance in determining the oxidative character of the atmosphere.

The primary aim of this study is fivefold: (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_2O_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; (iv) to understand the impact of MHP on the free radical cycle; and v) to evaluate the importance of MHP as an oxidant in the overall tropospheric oxidizing capacity.

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 BG site is a rural site located in the north of the central Pearl River Delta Region (PRD) and ~ 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 (~ 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 (~ 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 (~ 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 passed 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 ~ 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 ~ 50 %. The sampling inlet was mounted on the roof of a four-story building (~ 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. The ambient temperature ranged from 9 to 33 °C with an average value of 21 °C. The prevailing winds came from south or southeast with an average wind speed of 2 $m\,s^{-1}$.

2.2 Measurement method for MHP

A ground-based apparatus for measuring hydrogen peroxide and organic peroxides was set up by using 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. 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. The detection limit was 9 pptv for atmospheric H_2O_2 and 20 pptv for MHP. 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 Modeling methodology

A box model with the Carbon Bond Mechanism-Version IV (CBM-IV) developed by Gery et al. (1989) and updated by Adelman (1999) was performed. The CBM-IV mechanism includes 102 reactions concerning 40 species, with typical model inputs including solar radiation, temperature, water vapor, NO_x, SO_2, CO, and volatile organic compounds (VOCs). The box model assumed a well-mixed atmosphere to simplify the treatment of diffusion and transportation. Meteorological parameters, i.e., temperature, relative humidity, and mixing height were from observational data in PKU-summer 2006. The initial CO, SO_2, VOCs and NO_x concentrations input were representative of average concentrations in early morning in Beijing-summer 2006 with additional emissions every 1-h. The simulation was carried out on a 24-h basis and we chose the period from 24 h to 48 h for analysis.

3 Results and discussion

3.1 Ambient concentrations

Figure 1 shows 10 days of continuous MHP 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 2006/07/08, 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 Fig. 2a. A clear diurnal cycle, which can be explained by local photochemical production, was evident in BG-summer 2006, PKU-summer 2006/07/08, and MZ-summer 2007, but less distinct in YF-summer 2006 and PKU-winter 2007.

3.2 MHP/(MHP + H_2O_2) ratio

The MHP/(MHP+H_2O_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_2O_2 and MHP were often below the detection limit. Since the detection limit for MHP is higher than for H_2O_2, the calculated MHP/(MHP + H_2O_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 average MHP/(MHP + H_2O_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_2O_2) ratio in PKU-summer 2008 is shown in Fig. 3, together with corresponding H_2O_2 and MHP mixing ratios. The MHP/(MHP + H_2O_2) ratio was out phase with H_2O_2 and MHP mixing ratios, peaking during the night and early morning (~ 00:00–06:00) and decaying rapidly in the afternoon (~ 15:00–19:00).

The high values in the night and early morning indicate a preferential depletion of H_2O_2 to MHP, which can be attributed to both wet deposition and consumption by S(IV) in the aqueous phase. The high relative humidity (RH) during nighttime accelerates two H_2O_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_3O_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_2O_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_2O_2 to NO variations. In PKU-summer 2008, the average $\text{MHP}/(\text{MHP} + H_2O_2)$ ratio was higher than that in PKU-summer 2007, although the two 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 in urban Beijing (Wang et al., 2009). The average NO_x concentration decreased from 32.3 ppbv in PKU-summer 2007 (3–30 August) to 23.8 ppbv in PKU-summer 2008 (13 July–30 August). This suggests a transition from a H_2O_2 dominated regime to an organic peroxide dominated regime with decreasing NO_x. Considering the different roles of MHP and H_2O_2 in the atmospheric oxidizing capacity and the formation of secondary sulfates, this transition 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 ± 2.4 °C ambient temperature, 57.5 ± 9.3 % ambient relative humidity, 1001.4 ± 0.7 hPa ambient pressure, and 1.5 ± 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 ± 0.9 °C ambient temperature, 55.2 ± 9.2 % ambient relative humidity, 1006.1 ± 0.7 hPa ambient pressure, and 1.6 ± 1.7 $\mathrm{m\,s^{-1}}$ local wind speed. The MHP formation via the combination of HO_2 and CH_3O_2 radicals was investigated based on the observed free radical mixing ratios, as shown in Fig. 4. The average production rates of MHP from the reaction of CH_3O_2 with HO_2 for Case 1 and Case 2 can be calculated as 0.39 and 0.077 $\mathrm{ppbv\,h^{-1}}$, 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 1, the average MHP production rates from the ozonolysis of these alkenes for the two cases were 0.0063 and 0.0083 $\mathrm{ppbv\,h^{-1}}$, 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 2), photolysis (Reaction 3), and deposition. Considering the absorption cross sections of MHP are close to that of H_2O_2 (Finlayson-Pitts and Pitts Jr., 2000), the measured photolysis frequency of H_2O_2 was used in the calculation. The deposition rate coefficient of MHP was estimated to be $0.8 \times 10^{-5}\,\mathrm{s^{-1}}$ according to

Weller et al. (2000). For Case 1, the MHP loss rates through OH-reaction, photolysis and deposition were 0.065, 0.0075, and 0.0086 ppbv h^{-1}, respectively. For Case 2, the MHP loss rates were 0.0023 ppbv h^{-1} by OH-reaction, 0.00037 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 ~ 0.31 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_3O_2 and HO_2 does not yield 100 % MHP, but undergoes other channels to yield either HCHO (Reaction 1b) and CH_3OH (Reaction 1c). The branching ratio for Reaction (1a) 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. 5. In many atmospheric models, the reaction between CH_3O_2 and HO_2 is assumed to proceed exclusively by Reaction 1a (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.

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. 6, 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 (~ 120 ppbv) at the same time, which would substantially consume HO_2 and CH_3O_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, 2006), a 48-h-back trajectory reaching PKU site at 20:00 18 January (green line), 08:00 19 January (red line), and 20:00 19 January 2007 (blue line), obtained from NOAA (www.arl.noaa.gov) is shown in Fig. 7. The air mass reaching PKU site at 08:00 and 20:00 19 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 20:00 18 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_3I is considered 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 free radical budget and the atmospheric oxidizing capacity

MHP is considered as an index of the free radical (OH, HO_2 and CH_3O_2) concentrations. Here we present a preliminary evaluation of the sensitivities of free radical concentrations to the change of MHP chemistry using a box model with CBM-IV mechanism. The box model assumes a well-mixed atmosphere to represent chemical mechanisms in great detail. Two versions are implemented: Version-1 (original CBM-IV mechanism) and Version-2 (MHP kinetics, including MHP formation from the radical combination, Reaction 1a, oxidation by OH radical, Reaction 2a, b, and the photolysis, Reaction 3, are removed). The modeling results in terms of OH, HO_2 and CH_3O_2 concentrations are shown in Fig. 8. It can be seen that the OH and HO_2 concentrations simulated in Version-1 are almost the same as those in Version-2. However, there is a significant increase in CH_3O_2 concentration when MHP kinetics are removed from the CBM-IV mechanism, increasing concentration maxima by ~ 40 %.

The relative importance of MHP as an atmospheric oxidant is examined according to the "Counter Species" concept proposed by Leone and Seinfeld (1984). Counter species are fictitious products 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. They are produced only in one reaction and are not consumed. So they can count the number of times for a specific reaction that occurred until any time t. We added 67 counter species (C1–C67) in the CBM-IV mechanism to track the flows of several important oxidants in the atmosphere. Many species in the atmosphere can oxidize NO to NO_2, causing the accumulation of O_3 and consequently higher atmospheric oxidizing capacity. We use the ability of converting NO to NO_2 as an indicator to evaluate the contribution of individual oxidants to the atmospheric oxidizing capacity. 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:

$$F_s = \frac{\text{number of NO/NO}_2\text{ conversions due to produced species } S\text{, up to time } t}{\text{number of molucules } S \text{ formed, up to time } t} \tag{4}$$

The F 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. Note that since the formation of MHP by the ozonolysis of alkenes is not included in the current mechanism, the contribution of MHP to the overall atmospheric oxidizing capacity was potentially underestimated.

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_2O_2) ratio: (i) the diurnal variation of the MHP/(MHP+H_2O_2) ratio is out phase of the temporal profiles of H_2O_2 and MHP, indicating a preferential depletion of H_2O_2 to MHP during the night and early morning; and (ii) the elevated MHP/(MHP+H_2O_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_2O_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 influence of MHP on the radical budget is preliminarily accessed using a box model with CBM-IV mechanism. The simulation results suggest that MHP acts as a reservoir for OH and HO_2, but accounts for a significant sink for CH_3O_2. The importance of MHP as an atmospheric oxidant was evaluated using the "Counter Species" concept. The oxidizing capacity of MHP is ~ 4–5 times lower than free radicals such as OH, HO_2, and RO_2, but at the same level as HCHO and H_2O_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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Table 1. 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 × 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

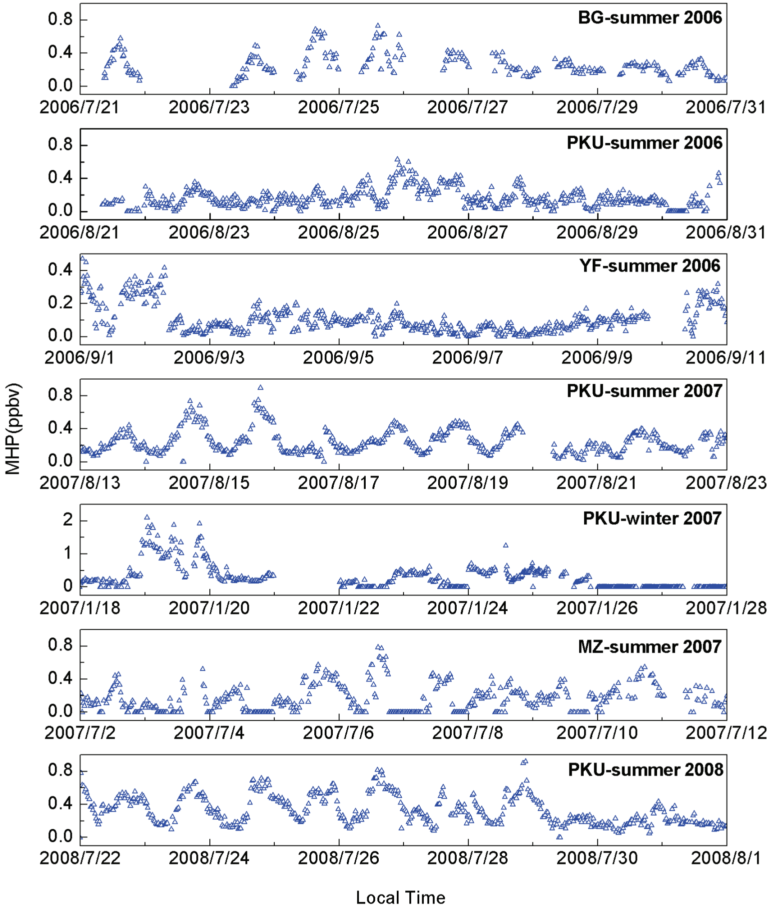

Fig. 1. Temporal profiles of atmospheric MHP during seven observations: BG-summer 2006, PKU-summer 2006, YF-summer 2006, MZ-summer 2007, PKU-summer 2007, PKU-winter 2007, and PKU-summer 2008.

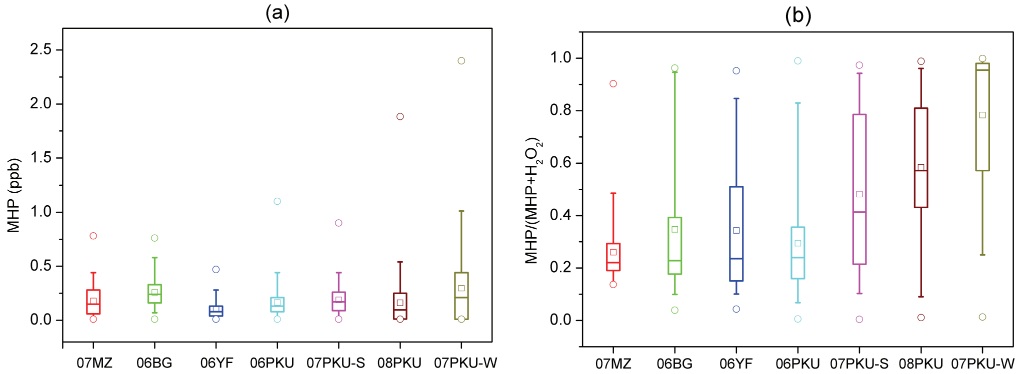

Fig. 2. MHP distribution (2a) and MHP/(MHP + H_2O_2) ratio (2b) during the seven observations: MZ-summer 2007 (07MZ), 30 June–31 July; BG-summer 2006 (06BG), 18–30 July; YF-summer 2006 (06YF), 1–12 September; PKU-summer 2006 (06PKU), 11–30 August; PKU-summer 2007 (07PKU-S), 3–30 August; PKU-summer 2008 (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.

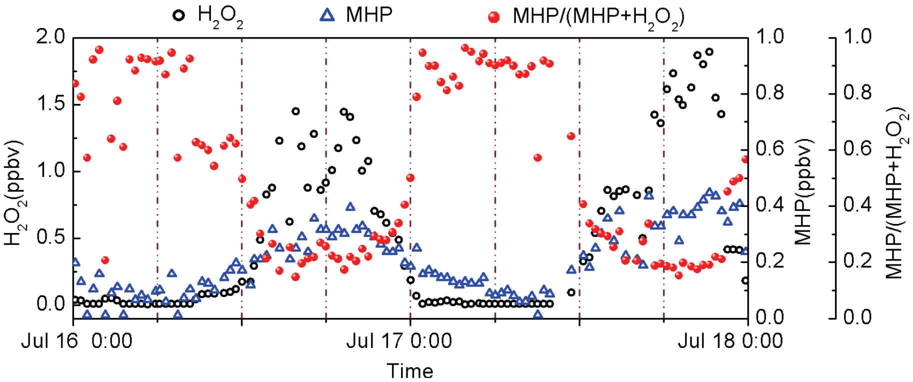

Fig. 3. MHP/(MHP + H_2O_2) ratio, together with concentrations of MHP and H_2O_2 in PKU-summer 2008.

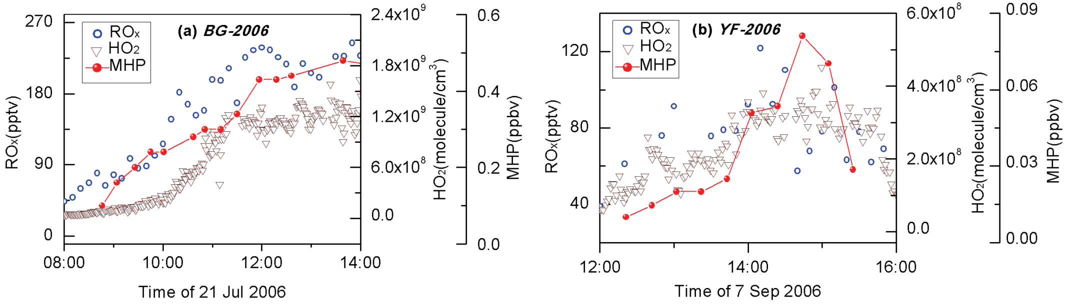

Fig. 4. Profiles of HO_2, RO_x (OH, HO_2, RO, and RO_2) and MHP concentrations measured at BG site on 21 July 2006 and at YF site on 9 September 2006.

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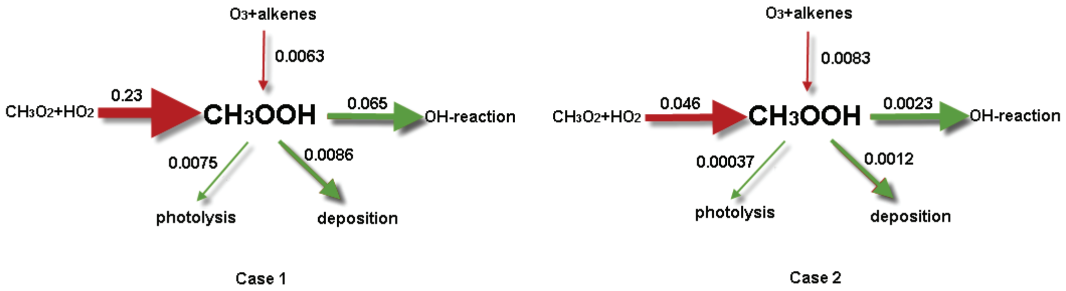

Fig. 5. Calculated sources and sinks of MHP (ppbv h^{-1}) for Case 1 (09:30–12:30 on 21 July in BG-summer 2006) and Case 2 (13:20–14:40 on 7 September 2006 in YF-summer 2006).

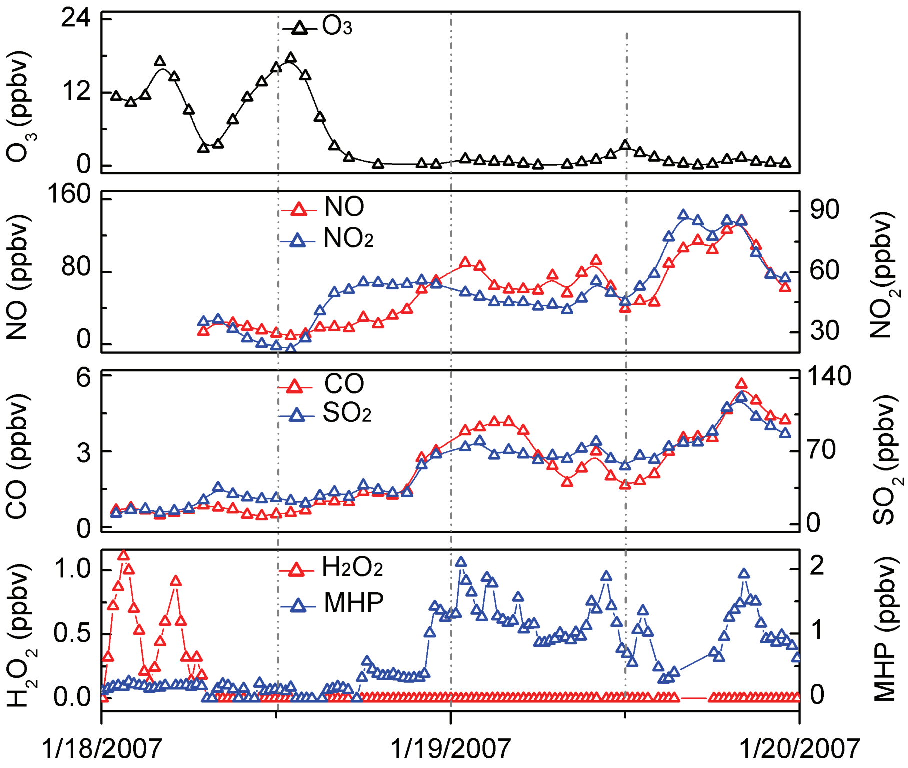

Fig. 6. Profiles of H_2O_2, MHP, CO, SO_2, NO, NO_2 and O_3 concentrations at PKU site on 18 and 19 January 2007.

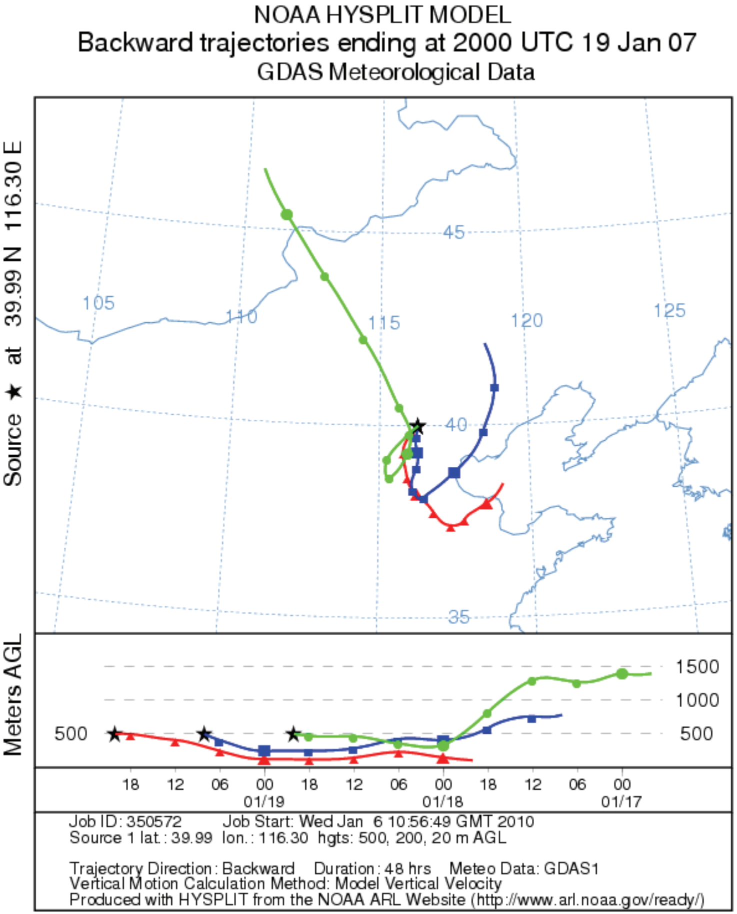

Fig. 7. 48-h-back trajectories reaching PKU site at 20:00 19 January (red line), 08:00 19 January (blue line), and 20:00 18 January 2007 (green line).

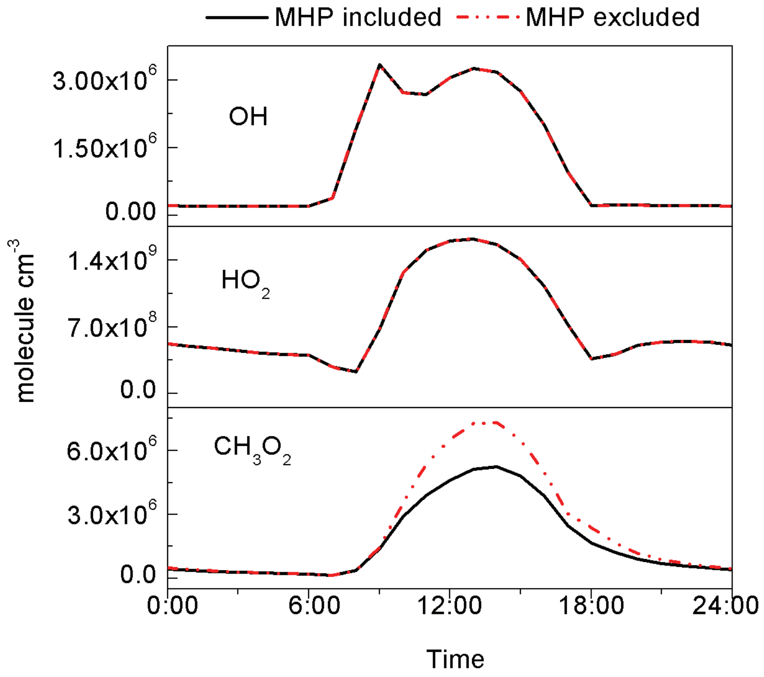

Fig. 8. The box model simulation of concentrations of free radicals before and after the MHP kinetics added to the CBM-IV mechanism.

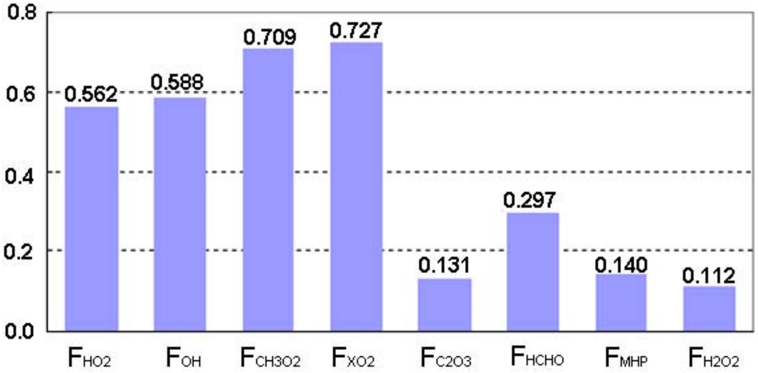

Fig. 9. *F* values of several important oxidants in the atmosphere after 72 h simulation.