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# Methyl hydroperoxide (CH<sub>3</sub>OOH) in urban, suburban and rural atmosphere: ambient concentration, budget, and contribution to the atmospheric oxidizing capacity

X. Zhang<sup>1,\*</sup>, S. Z. He<sup>1</sup>, Z. M. Chen<sup>1</sup>, Y. Zhao<sup>1</sup>, and W. Hua<sup>1</sup>

<sup>1</sup>State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China  
\* now at: Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, CA 91125, USA

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Correspondence to: Z. M. Chen (zmchen@pku.edu.cn)

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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<sub>2</sub>O<sub>2</sub>) ratio is also presented here to examine different sensitivities of MHP and H<sub>2</sub>O<sub>2</sub> to certain atmospheric processes. The diurnal cycle of MHP/(MHP+H<sub>2</sub>O<sub>2</sub>), which is out of phase with the diurnal cycle of both H<sub>2</sub>O<sub>2</sub> and MHP, could imply that MHP production is more sensitive to the ambient NO concentration, while H<sub>2</sub>O<sub>2</sub> 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<sub>3</sub>O<sub>2</sub> radical 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;

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### 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  $\pm$  standard deviation) were:  $32.3 \pm 2.4$  °C ambient temperature,  $57.5 \pm 9.3$  % ambient relative humidity,  $1001.4 \pm 0.7$  hPa ambient pressure, and  $1.5 \pm 0.9$  ms<sup>-1</sup> local wind speed. Case 2 was a cloudy day and the average meteorological parameters (arithmetic mean  $\pm$  standard deviation) were:  $25.7 \pm 0.9$  °C ambient temperature,  $55.2 \pm 9.2$  % ambient relative humidity,  $1006.1 \pm 0.7$  hPa ambient pressure, and  $1.6 \pm 1.7$  ms<sup>-1</sup> local wind speed. The MHP formation via the combination of HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> 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<sub>3</sub>O<sub>2</sub> with HO<sub>2</sub> for Case 1 and Case 2 can be calculated as 0.39 and 0.077 ppbv h<sup>-1</sup>, 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 ppbv h<sup>-1</sup>, 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<sub>2</sub>O<sub>2</sub> (Finlayson-Pitts and Pitts Jr., 2000), the measured photolysis frequency of H<sub>2</sub>O<sub>2</sub> was used in the calculation. The deposition rate coefficient of MHP was estimated to be  $0.8 \times 10^{-5}$  s<sup>-1</sup> according to

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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<sup>-1</sup>, respectively. For Case 2, the MHP loss rates were 0.0023 ppbv h<sup>-1</sup> by OH-reaction, 0.00037 ppbv h<sup>-1</sup> by photolysis, and 0.0012 ppbv h<sup>-1</sup> by deposition.

Balancing the MHP production and removal pathways, from above gives a net increase of  $\sim 0.31$  and  $\sim 0.081$  ppbv h<sup>-1</sup> for Case 1 and Case 2, respectively. However the observed increase rates of MHP were lower, at  $\sim 0.11$  and  $\sim 0.061$  ppbv h<sup>-1</sup>, respectively. To understand this overestimation, consider that the reaction between CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> does not yield 100 % MHP, but undergoes other channels to yield either HCHO (Reaction 1b) and CH<sub>3</sub>OH (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  $\sim 60$  % MHP yield leads to a better agreement with the observational values, see Fig. 5. In many atmospheric models, the reaction between CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub> 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<sub>x</sub> cycling and O<sub>3</sub> 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 ( $\sim 120$  ppbv) at the same time, which would substantially consume HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> and as a result suppress the formation of MHP. The second MHP formation pathway,

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most of the remaining NO to NO<sub>2</sub> conversion is due to HCHO. The percent of NO to NO<sub>2</sub> conversion due to H<sub>2</sub>O<sub>2</sub> chemistry is about the same as the percent conversion due to MHP chemistry. The contribution of MHP to the NO/NO<sub>2</sub> conversion is ~ 1/4 that of HO<sub>2</sub>. 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<sub>2</sub>O<sub>2</sub>) ratio: (i) the diurnal variation of the MHP/(MHP+H<sub>2</sub>O<sub>2</sub>) ratio is out phase of the temporal profiles of H<sub>2</sub>O<sub>2</sub> and MHP, indicating a preferential depletion of H<sub>2</sub>O<sub>2</sub> to MHP during the night and early morning; and (ii) the elevated MHP/(MHP+H<sub>2</sub>O<sub>2</sub>) ratios in PKU-summer 2008, when mitigation of atmospheric pollution was implemented in Beijing, suggests that MHP is more sensitive to NO than H<sub>2</sub>O<sub>2</sub>. 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<sub>2</sub>, but accounts for a significant sink for CH<sub>3</sub>O<sub>2</sub>. 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<sub>2</sub>, and RO<sub>2</sub>, but at the same level as HCHO and H<sub>2</sub>O<sub>2</sub>. Note that the photochemical box model simulated

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a typical urban atmosphere in this study. Apparently, the impact of MHP on the free radical cycle should be more significant under low NO<sub>x</sub> environment, where RO<sub>2</sub> + HO<sub>2</sub> instead of RO<sub>2</sub> + 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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#### References

- Adelman, Z. E.: A reevaluation of the carbon bond-IV photochemical mechanism, Master's Thesis, Department of Environmental Engineering, University of North Carolina at Chapel-Hill, NC, 1999.
- Amouroux, D., Roberts, G., Rapsomanikis, S., and Andreae, M. O.: Biogenic gas (CH<sub>4</sub>, N<sub>2</sub>O, DMS) emission to the atmosphere from near-shore and shelf waters of the Northwestern Black Sea, *Est. Coast. Shelf Sci.*, 54, 575–587, 2002.
- Atkinson, R., Baulch, D. L., Cox, R. A., Hampson Jr., R. F., Kerr, J. A., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry, organic species: supplement VII, *J. Phys. Chem. Ref. Data*, 28, 191–393, 1999.
- Avzianova, E. V. and Ariya, P. A.: Temperature-dependent kinetic study for ozonolysis of selected tropospheric alkenes, *Int. J. Chem. Kinet.*, 34, 678–684, 2002.
- Bell, N., Hsu, L., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lobert, J. M., and Maier-Reimer, E.: Methyl iodide: atmospheric budget and use as a tracer of marine convection in global models, *J. Geophys. Res.*, 107, 4340, doi:10.1029/2001JD001151, 2002.

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- Böge, O., Miao, Y., Plewka, A., and Herrmann, H.: Formation of secondary organic particulate phase compounds from isoprene gas-phase oxidation products: an aerosol chamber and field study, *Atmos. Environ.*, 40, 2501–2509, 2006.
- Calvert, J. G., Lazrus, A., Kok, G. L., Heikes, B. G., Walega, J. G., Lind, J., and Cantrell, C. A.: Chemical mechanisms of acid generation in the troposphere, *Nature*, 317, 27–35, 1985.
- Chen, C. T. A. and Tseng, H. C.: Abnormally high CH<sub>4</sub> concentrations in seawater at mid-depths on the continental slopes of the northern South China Sea, *Terr. Atmos. Ocean. Sci.*, 17, 951–959, 2006.
- Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencsér, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmos. Environ.*, 38, 4093–4098, 2004.
- Cohan, D. S., Schultz, M. G., and Jacob, D. J.: Convective injection and photochemical decay of peroxides in the tropical upper troposphere: methyl iodide as a tracer of marine convection, *J. Geophys. Res.*, 104, 5717–5724, 1999.
- Elrod, M. J., Ranschaert, D. L., and Schneider, N. J.: Direct kinetics study of the temperature dependence of the CH<sub>2</sub>O branching channel for the CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> reaction, *Int. J. Chem. Kinet.*, 33, 363–376, 2001.
- Enami, S., Yamanaka, T., and Kawasaki, M.: Near-infrared cavity ring-down spectroscopic study of the reaction of methylperoxy radical with nitrogen monoxide, *Chem. Lett.*, 38, 80–81, 2009.
- Finlayson-Pitts, B. J. and Pitts Jr., J. N.: *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press, San Diego, 2000.
- Frey, M. M., Stewart, R. W., McConnell, J. R., and Bales, R. C.: Atmospheric hydroperoxides in west Antarctica: links to stratospheric ozone and atmospheric oxidation capacity, *J. Geophys. Res.*, 110, D23301, doi:10.1029/2005JD006110, 2005.
- Gäb, S., Hellpointner, E., Turner, W. V., and Korte, F.: Hydroxymethyl hydroperoxide and bis (hydroxymethyl) peroxide from gas-phase ozonolysis of naturally occurring alkenes, *Nature*, 316, 535–536, 1985.
- Gäb, S. E., Yurner, W. V., Wolff, S., Becker, K. H., Puppert, L., and Brockmann, L. J.: Formation of alkyl and hydroxyalkyl hydroperoxides on ozonolysis in water and in air, *Atmos. Environ.*, 29, 2401–2407, 1995.
- Gery, M. W., Whitten, G. Z., Killus, J. P., and Dodge, M. C.: A photochemical kinetics mechanism for urban and regional scale computer modeling, *J. Geophys. Res.*, 94, 12925–12956, 1989.

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- Grosjean, E. and Grosjean, D.: Rate constants for the gas-phase reaction of ozone with 1, 1-disubstituted alkenes, *Int. J. Chem. Kinet.*, 28, 911–918, 1996.
- Grossmann, D., Moortgat, G. K., Kibler, M., Schlomski, S., Bachmann, K., Alicke, B., Geyer, A., Platt, U., Hammer, M. U., Vogel, B., Mihelcic, D., Hofzumahaus, A., Holland, F., and Volz-Thomas, A.: Hydrogen peroxide, organic peroxides, carbonyl compounds, and organic acids measured at Pabstthum during BERLIOZ, *J. Geophys. Res.*, 108, 8250, doi:10.1029/2001JD001096, 2003.
- Hauglustaine, D. A., Granier, C., Brasseur, G. P., and Megie, G.: The importance of atmospheric chemistry in the calculation of radiative forcing on the climate system, *J. Geophys. Res.*, 99, 1173–1186, 1994.
- He, S. Z., Chen, Z. M., Zhang, X., Zhao, Y., Huang, D. M., Zhao, J. N., Zhu, T., Hu, M., and Zeng L. M.: Measurement of atmospheric hydrogen peroxide and organic peroxides in Beijing before and during the 2008 Olympic Games: chemical and physical factors influencing their concentrations, *J. Geophys. Res.*, 115, D17307, doi:10.1029/2009JD013544, 2010.
- Heikes, B., Lee, M., Jacob, D., Talbot, R., Bradshaw, J., Singh, H., Blake, D., Anderson, B., Fuelberg, H., and Thompson, A. M.: Ozone, hydroperoxide, oxides of nitrogen, and hydrocarbon budgets in the marine boundary layer over the South Atlantic, *J. Geophys. Res.*, 101, 24221–24234, 1996.
- Hewitt, C. N. and Kok, G. L.: Formation and occurrence of organic hydroperoxides in the troposphere: laboratory and field observations, *J. Atmos. Chem.*, 12(2), 181–194, 1991.
- Hewitt, C. N., Kok, G. L., and Fall, R.: Hydroperoxides in plants exposed to ozone mediate air pollution damage to alkene emitters, *Nature*, 344, 56–58, 1990.
- Heyer, J. and Berger, U.: Methane emission from the coastal area in the southern baltic sea, *Est. Coast. Shelf Sci.*, 51(1), 13–30, 2000.
- Hua, W., Chen, Z. M., Jie, C. Y., Kondo, Y., Hofzumahaus, A., Takegawa, N., Chang, C. C., Lu, K. D., Miyazaki, Y., Kita, K., Wang, H. L., Zhang, Y. H., and Hu, M.: Atmospheric hydrogen peroxide and organic hydroperoxides during PRIDE-PRD'06, China: their concentration, formation mechanism and contribution to secondary aerosols, *Atmos. Chem. Phys.*, 8, 6755–6773, doi:10.5194/acp-8-6755-2008, 2008.
- Horie, O., Neeb, P., Limbach, S., and Moortgat, G.: Formation of formic acid and organic peroxides in ozonolysis of ethene with added water vapour, *Geophys. Res. Lett.*, 21, 1523–1526, 1994.

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- Jaeglé, L., Jacob, D. J., Wennberg, P. O., Spivakovsky, C. M., Hanisco, T. F., Lanzendorf, E. J., Hints, E. J., Fahey, D. W., Keim, E. R., Proffitt, M. H., Atlas, E. L., Flocke, F., Schauffler, S., McElroy, C. T., Midwinter, C., Pfister, L., and Wilson, J. C.: Observed OH and HO<sub>2</sub> in the upper troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, 24, 3181–3184, 1997.
- 5 Jenkin, M. E., Cox, R. A., Hayman, G. D., and Whyte, L. J.: Kinetic study of the reactions CH<sub>3</sub>O<sub>2</sub>+CH<sub>3</sub>O<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>+HO<sub>2</sub> using molecular modulation spectroscopy, *J. Chem. Soc., Faraday Trans.*, 84, 913–930, 1988.
- Khamaganov, V. G. and Hites, R. A.: Rate constants for the gas-phase reactions of ozone with isoprene,  $\alpha$ - and  $\beta$ -pinene, and limonene as a function of temperature, *J. Phys. Chem. A*, 105, 815–822, 2001.
- 10 Klippel, T., Fischer, H., Bozem, H., Lawrence, M. G., Butler, T., Jöckel, P., Tost, H., Martinez, M., Harder, H., Regelin, E., Sander, R., Schiller, C. L., Stickler, A., and Lelieveld, J.: Distribution of hydrogen peroxide and formaldehyde over Central Europe during the HOOVER project, *Atmos. Chem. Phys.*, 11, 4391–4410, doi:10.5194/acp-11-4391-2011, 2011.
- 15 Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.
- Lee, M., Heikes, B. G., and Jacob, D. J.: Enhancements of hydroperoxides and formaldehyde in biomass impacted air and their effect on atmospheric oxidant cycles, *J. Geophys. Res.*, 103, 13201–13212, 1998.
- Leone, J. A. and Seinfeld, J. H.: Analysis of the characteristics of complex chemical reaction mechanisms: application to photochemical smog chemistry, *Environ. Sci. Technol.*, 18, 280–287, 1984.
- 25 Li, H. J., Yokouchi, Y., Akimoto, H., and Narita, Y.: Distribution of methyl chloride, methyl bromide, and methyl iodide in the marine boundary air over the western Pacific and southeastern Indian Ocean, *Geochem. J.*, 35, 137–144, 2001.
- Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destiau, M., Hayman, G. D., Jenkin, M. E., Moortgat, G. K., and Zabel, F.: Organic peroxy radicals: kinetics, spectroscopy and tropospheric chemistry, *Atmos. Environ.*, 26, 1805–1961, 1992.
- 30 Lind, J. A. and Kok, G. L.: Correction to ‘Henry’s law determinations for aqueous solutions of hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid’, *J. Geophys. Res.*, 99, 21119–21119, 1994.

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- Madronich, S. and Calvert, J. G.: permutation reactions of organic peroxy radicals in the troposphere, *J. Geophys. Res.*, 95, 5697–5715, 1999.
- Mari, C., Jacob, D. J., and Bechthold, P.: Transport and scavenging of soluble gases in a deep convective cloud, *J. Geophys. Res.*, 105, 22255–22267, 2000.
- 5 Martin, L. R. and Damschen, D. E.: Aqueous oxidation of sulfur-dioxide by hydrogen-peroxide at low pH, *Atmos. Environ.*, 15, 1615–1621, 1981.
- O’Sullivan, D. W., Heikes, B. G., Lee, M., Chang, C., Gregory, G., Blake D., and Sachse, G.: The distribution of hydrogen peroxide and methyl hydroperoxide in the Pacific and South Atlantic, *J. Geophys. Res.*, 104, 5635–5646, 1999.
- 10 Pandis, S. N. and Seinfeld, J. H.: Sensitivity analysis study of a chemical mechanism for aqueous-phase atmospheric chemistry, *J. Geophys. Res.*, 94, 1105–1126, 1989.
- Penkett, S. A., Jones, B. M. R., Brice, K. A., and Eggleton, A. E. J.: Importance of atmospheric ozone and hydrogen-peroxide in oxidizing sulfur-dioxide in cloud and rainwater, *Atmos. Environ.*, 13, 123–137, 1979.
- 15 Polle, A. and Jundermann, W.: Does atmospheric hydrogen peroxide contribute to damage to forest trees?, *Environ. Sci. Technol.*, 28, 812–815, 1994a.
- Polle, A. and Jundermann, W.: Inhibition of apoplastic and symplastic peroxidase activity from Norway spruce by the photooxidant hydroxymethyl hydroperoxide, *Plant Physiol.*, 104, 617–621, 1994b.
- 20 Ravetta, F., Jacob, D. J., Brune, W. H., Heikes, B. G., Anderson, B. E., Blake, D. R., Gregory, G. L., Sachse, G. W., Sandholm, S. T., Shetter, R. E., Singh, H. B., and Talbot, R. W.: Experimental evidence for the importance of convected methylhydroperoxide as a source of hydrogen oxide (HO<sub>x</sub>) radicals in the tropical upper troposphere, *J. Geophys. Res.*, 106, 32709–32716, 2001.
- 25 Rehder, G., Collier, R. W., Heeschen, K., Kosro, P. M., Barth, J., and Suess, E.: Enhanced marine CH<sub>4</sub> emissions to the atmosphere off Oregon caused by coastal upwelling, *Global Biogeochem. Cy.*, 16, 1081, doi:10.1029/2000GB001391, 2002.
- Riedel, K., Weller, R., Schrems, O., and König-Langlo, G.: Variability of tropospheric hydroperoxides at a coastal surface site in Antarctica, *Atmos. Environ.*, 34, 5225–5234, 2000.
- 30 Schmale, O., Greinert, J., and Rehder, G.: Methane emission from high-intensity marine gas seeps in the Black Sea into the atmosphere, *Geophys. Res. Lett.*, 32, L07609, doi:10.1029/2004GL021138, 2005.

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- Slemr, F. and Tremmel, H. G.: Hydroperoxides in the marine troposphere over the Atlantic Ocean, *J. Atmos. Chem.*, 19, 371–404, 1994.
- Snow, J. A., Heikes, B. G., Shen, H. W., O'Sullivan, D. W., Fried, A., and Walega, J.: Hydrogen peroxide, methyl hydroperoxide, and formaldehyde over North America and the North Atlantic, *J. Geophys. Res.*, 112, D12S07, doi:10.1029/2006JD007746, 2007.
- 5 Treacy, J., Elhag, M., O'Farrell, D., and Sidebottom, H.: Reactions of ozone with unsaturated organic compounds, *Ber. Bunsenges. Phys. Chem. Chem. Phys.*, 96, 422–427, 1992.
- Valverde-Canossa, J., Wieprecht, W., Acher, K., and Moortgat, G. K.: H<sub>2</sub>O<sub>2</sub> and organic peroxide measurements in an orographic cloud: The FEBUKO experiment, *Atmos. Environ.*, 39, 4279–4290, 2005.
- 10 Wallington, T. J.: Fourier-transform infrared product study of the reaction of CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> over the pressure range 15–700 Torr at 295 K, *J. Chem. Soc., Faraday Trans.*, 87, 2379–2382, 1991.
- Wallington, T. J., Dagaut, P., and Kurylo, M. J.: Ultraviolet-absorption cross-sections and reaction-kinetic and mechanisms for peroxy-radicals in the gas-phase, *Chem. Rev.*, 92, 667–710, 1992.
- 15 Wang, C. X. and Chen, Z. M.: Effect of CH<sub>3</sub>OOH on the atmospheric concentration of OH radicals, *Prog. Nat. Sci.*, 16, 1141–1149, 2006.
- Wang, Y., Hao, J., McElroy, M. B., Munger, J. W., Ma, H., Chen, D., and Nielsen, C. P.: Ozone air quality during the 2008 Beijing Olympics: effectiveness of emission restrictions, *Atmos. Chem. Phys.*, 9, 5237–5251, doi:10.5194/acp-9-5237-2009, 2009.
- 20 Wegener, R., Brauers, T., Koppmann, R., Bares, S. R., Rohrer, F., Tillmann, R., Wahner, A., Hansel, A., and Wisthaler, A.: Simulation chamber investigation of the reactions of ozone with short-chained alkenes, *J. Geophys. Res.*, 112, D13301, doi:10.1029/2006JD007531, 2007.
- 25 Weller, R. and Schrems, O.: H<sub>2</sub>O<sub>2</sub> in the marine troposphere and seawater of the Atlantic Ocean (48° N–63° S), *Geophys. Res. Lett.*, 20, 125–128, 1993.
- Weller, R., Schrems, O., Boddenberg, A., Gäb, S., and Gautrois, M.: Meridional distribution of hydroperoxides and formaldehyde in the marine boundary layer of the Atlantic (48° N–35° S) measured during the Albatross campaign, *J. Geophys. Res.*, 105, 14401–14412, 2000.
- 30 Weinstein-Lloyd, J. B., Lee, L. J., Daum, P. H., Kleinmann, L. I., Nunnermacker, L. J., and Springston, S. R.: Measurement of peroxides and related species during the 1995 summer intensive of the Southern Oxidants Study in Nashville, Tennessee, *J. Geophys. Res.*, 103, 22361–22373, 1998.

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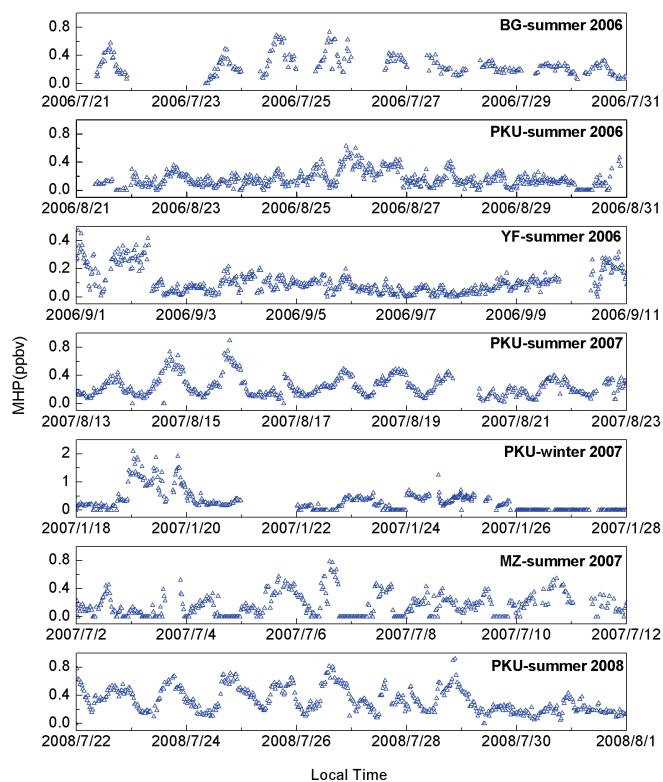
- Xu, J. R. and Chen, Z. M.: Determination of peroxides in environmental samples by high performance liquid chromatography with fluorescence detection, *Chinese J. Chromatogr.*, 23, 366–369, 2005.
- 5 Yokouchi, Y., Nojiri, Y., Barrie, L. A., Toom-Sauntry, D., and Fujinuma, Y.: Atmospheric methyl iodide: high correlation with surface seawater temperature and its implications on the sea-to-air flux, *J. Geophys. Res.*, 106, 12661–12668, 2001.
- Zhang, X., Chen, Z. M., He, S. Z., Hua, W., Zhao, Y., and Li, J. L.: Peroxyacetic acid in urban and rural atmosphere: concentration, feedback on PAN-NO<sub>x</sub> cycle and implication on radical chemistry, *Atmos. Chem. Phys.*, 10, 737–748, doi:10.5194/acp-10-737-2010, 2010.

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**Table 1.** Reaction rates of 12 C<sub>2</sub>–C<sub>5</sub> alkenes with O<sub>3</sub> 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).

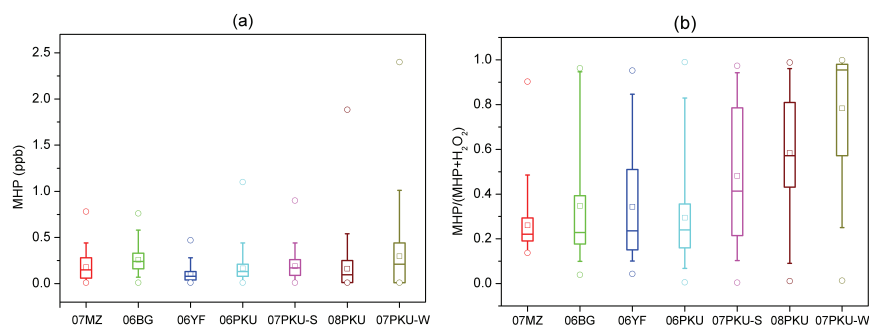
Alkenes	Rate coefficient × 10 <sup>-18</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Reference	Concentration (ppbv)		Rate (ppbv h <sup>-1</sup> )	
			Case 1	Case 2	Case 1	Case 2
Ethene	1.7	Atkinson et al. (1999)	3.41	3.43	0.0200	0.038
Propene	10.6		1.00	0.61	0.0360	0.042
Trans-2-Butene	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

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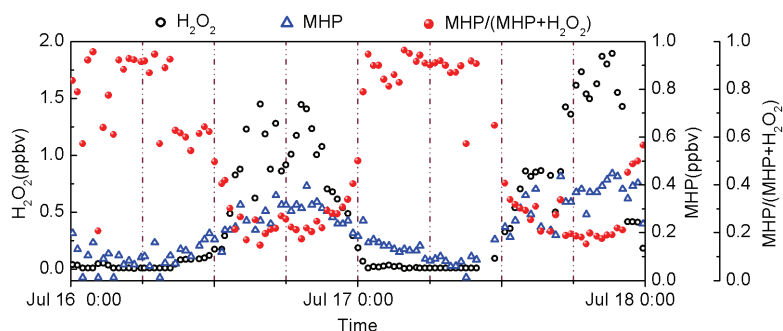
**Fig. 1.** Temporal profiles of atmospheric MHP during seven observations: BG-summer 2006, PKU-summer 2006, YF-summer 2006, MZ-summer 2007, PKU-summer 2007, PKU-winter 2007, and PKU-summer 2008.

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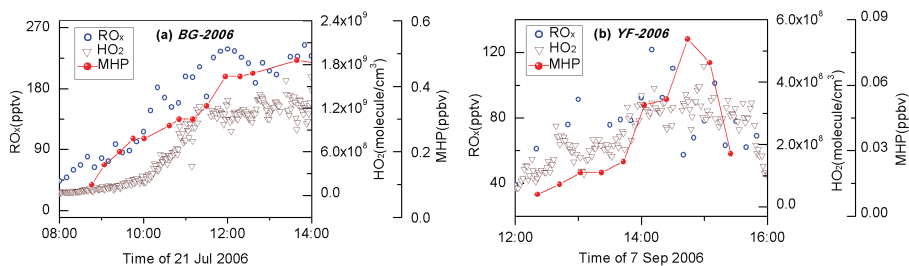
**Fig. 2.** MHP distribution (2a) and MHP/(MHP + H<sub>2</sub>O<sub>2</sub>) ratio (2b) during the seven observations: MZ-summer 2007 (07MZ), 30 June–31 July; BG-summer 2006 (06BG), 18–30 July; YF-summer 2006 (06YF), 1–12 September; PKU-summer 2006 (06PKU), 11–30 August; PKU-summer 2007 (07PKU-S), 3–30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

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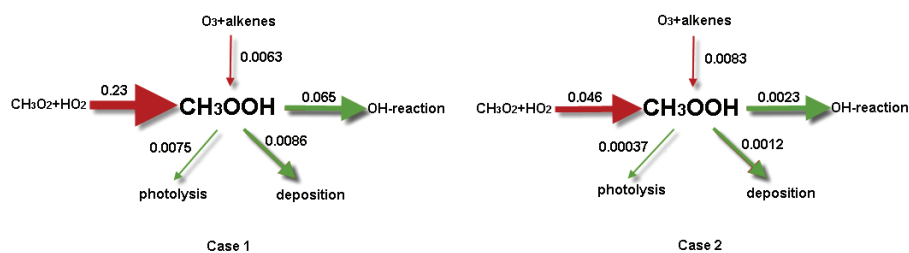
**Fig. 3.** MHP/(MHP + H<sub>2</sub>O<sub>2</sub>) ratio, together with concentrations of MHP and H<sub>2</sub>O<sub>2</sub> in PKU-summer 2008.

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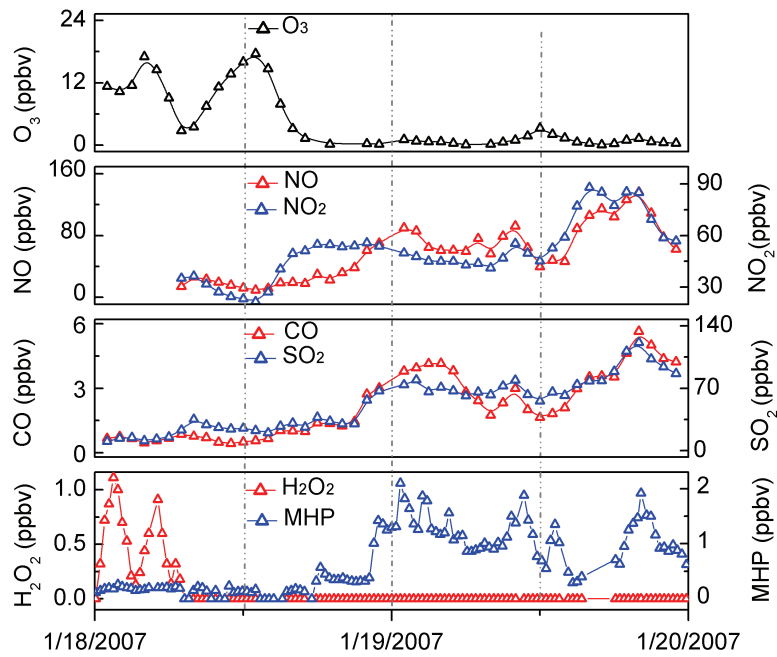
**Fig. 4.** Profiles of HO<sub>2</sub>, RO<sub>x</sub> (OH, HO<sub>2</sub>, RO, and RO<sub>2</sub>) and MHP concentrations measured at BG site on 21 July 2006 and at YF site on 9 September 2006.

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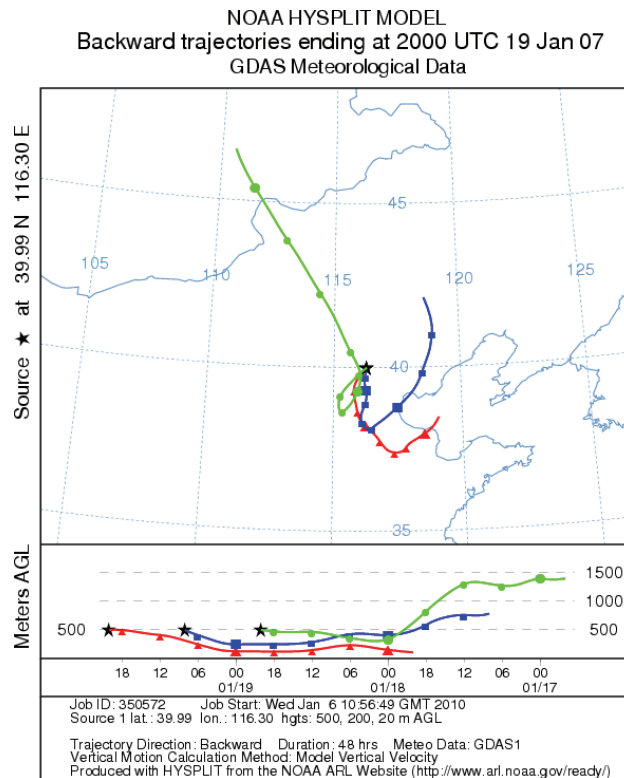
**Fig. 5.** Calculated sources and sinks of MHP (ppbv h<sup>-1</sup>) for Case 1 (09:30–12:30 on 21 July in BG-summer 2006) and Case 2 (13:20–14:40 on 7 September 2006 in YF-summer 2006).

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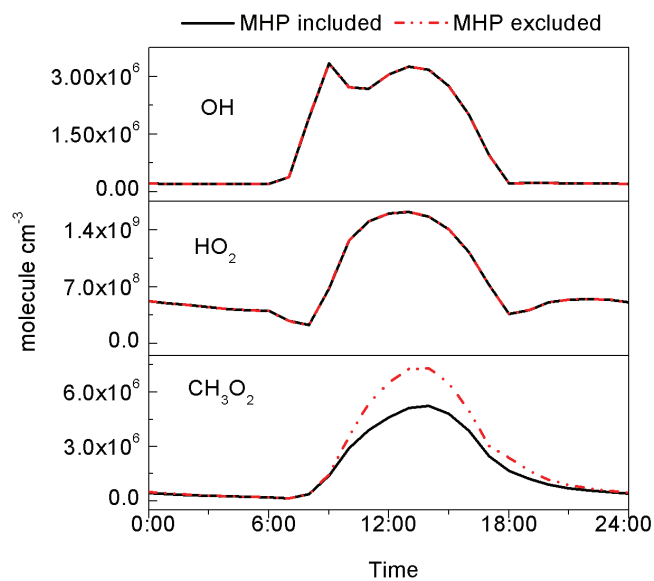
**Fig. 6.** Profiles of H<sub>2</sub>O<sub>2</sub>, MHP, CO, SO<sub>2</sub>, NO, NO<sub>2</sub> and O<sub>3</sub> concentrations at PKU site on 18 and 19 January 2007.

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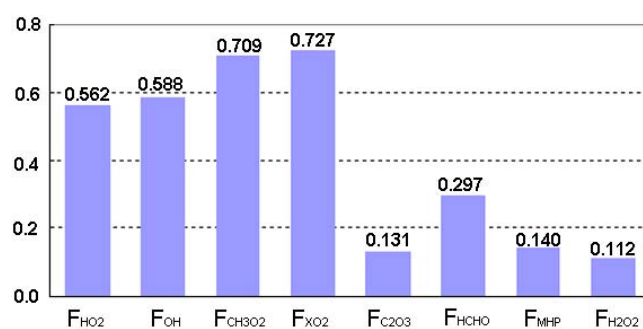
**Fig. 7.** 48-h-back trajectories reaching PKU site at 20:00 19 January (red line), 08:00 19 January (blue line), and 20:00 18 January 2007 (green line).

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

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

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