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Interactive comment on “Methyl hydroperoxide (CH₃OOH) in urban, suburban and rural atmosphere: ambient concentration, budget, and contribution to the atmospheric oxidizing capacity” by X. Zhang et al.

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General Comments

The authors present data and analysis of CH₃OOH (MHP) measurements from 7 field studies spanning 4 sites in China, including 3 summer field experiments in Beijing. The field observations typically lasted 20 days during summer months although some winter and fall measurements are also reported. The authors analyzed some of the data using a chemical box model running the carbon bond IV mechanism to simulate mea-

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sured CH_3OOH mixing ratios and its impact on “oxidation capacity”. The observations are of interest principally because CH_3OOH measurements are infrequently reported. The authors report that reductions in NO_x emissions in Beijing during the Olympics increased the MHP to total peroxide ratio, and that elevated MHP mixing ratios observed in winter (2 ppbv) could be traced to oceanic air mass influence. The principle problems with the paper are 1) an incomplete presentation of the data (i.e. no H_2O_2 data are shown) and 2) a very poor presentation of the box modeling work. I found the modeling analysis very incomplete and confusing and felt it didn't provide any new insight. The box modeling needs to be dramatically improved or removed from the paper. The modeled cases presented are not clearly motivated by scientific questions. A critical oversight with the modeling analysis is that it was not applied to understand one of the author's key observations – higher MHP / total peroxide ratios at lower NO mixing ratios in the Beijing data. Also the authors assumed that CH_3OOH photolysis rates are the same as H_2O_2 . This means J CH_3OOH is significantly overestimated, causing errors in the MHP budget analysis they present. The counter species analysis was very poorly presented. My recommendation is that the authors improve the presentation of the observations – these are worthy of the archival literature - and consider submitting the modeling effort as a more focused and more detailed effort in a separate publication.

Thanks for the reviewer's constructive and thoughtful comments. We have greatly revised our manuscript, according to the comments. Below is our response, as shown in answer (A), to the reviewer's comments.

Specific Concerns

P 13092. Your goal (v) to evaluate the importance of MHP as an oxidant in the overall tropospheric oxidizing capacity is not evaluated in this study. For that you need a global chemical transport model. This goal should be removed.

A: Yes, we have removed item (v).

P 13094. I found the description of the box model simulations very incomplete. Is

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this a 0-D box model? What were the boundary conditions used, how were emissions treated, what was the length of the simulation, was it run to steady state peroxide concentrations?

A: We have added description in Section, also shown below:

“...Meteorological parameters, i.e., radiation intensity, temperature, relative humidity, and mixing layer height were from 10 minutes average observational data from PKU-summer 2006. The initial CO, SO₂, NO_x, CH₄, 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 SO₂, respectively, every one minute. The simulation was carried out on a 24-h basis and we chose the period after 72 h for analysis.”

P 13095, Section 3.1. Why are only 10 days shown and not the entire measurement period of 20 days? I would suggest showing all the data unless there is some compelling reason not to. Why aren't the H₂O₂ data shown – these would be informative and should be added to the data presentation. Could Figure 1 be reorganized into multiple columns to contrast urban, suburban and rural sites? As displayed it is hard to see if there is a difference in peroxide levels between the sites. Potential differences in total peroxides due to NO_x concentration gradients between the sites would be of interest. Figure 2a is not very informative as the values of the bar and whisker plot can't be determined given the scale. Showing these data in a table would be more valuable to the reader.

A: Yes, we have added H₂O₂ on Figure 1. Urban measurements are shown in Figure 1a and rural sites are shown in Figure 1b. We added Table 2 to show the statistical distribution of MHP. We would still like to keep the Figure 2a as suggested by reviewers for ACPD.

The physical and chemical parameters affecting MHP levels in the atmosphere are complex. The influence of NO on MHP would only be obvious if all the other conditions

are similar. So it is not necessary to show NO_x levels in figure 1. In addition, we have already included NO_x levels in the discussion of Section 3.2. We only chose the typical ten days continuous data, which we thought are sufficient to reflect the atmospheric peroxides concentration, for each measurement. For reasons like facilities maintain, we might not have data acquired or any signal detected (e.g. the peroxides level was very low, near or under the detection limit, after Olympic started because of the pollutants control policy and rainy weather conditions). So we thought it is not necessary to report all the data we got and 10 days continuously measured data would be sufficient to reflect the average level and the general trend. We still would like to present all the data sets for the 7 measurements to the reviewer, as shown in figures 1 and 2 in the response. P 13095, Section 3.2. You need a new figure to demonstrate the statistical significance of the diurnal cycle of the peroxides (H_2O_2 and MHP). I suggest you plot average and median hourly values versus time of day. I would be interested in the differences in Beijing for the 3 summers to see the influence of lower NO_x in summer 2008.

A: We added a new figure (Figure 4) in the revised manuscript, showing the average hourly concentrations of peroxides versus time of day, and the influence of lower NO_x in summer 2008. We can see from Figure 4 that on Aug 15 2007 and Jul 23 2008, the CO concentrations, together with the meteorology conditions were consistent, whereas the NO concentration in the morning of August 15 2007 was substantially higher than July 23 2008. As a result, the $\text{MHP}/(\text{H}_2\text{O}_2+\text{MHP})$ ratio was much lower in the presence of high level of NO_x .

P 13095. MHP ratios. Since physical loss processes are dominant at night it would be better to separate the day and nighttime data to contrast MHP / total peroxide ratios amongst the sites. Comparing daytime data would allow for more solid conclusions about the role of local chemistry and NO_x/VOC ratios on the abundance of MHP. Why is such a limited time period shown in Figure 3? It would be more informative to show diurnal averages or medians for the 4 sites.

A: We would like to show a clearer diurnal profile of MHP in Figure 3, so we decided to only show two days' data. We would like to show the nighttime data too in Figure 3 because the removal processes for H_2O_2 are faster than those for MHP, which can be reflected by $\text{MHP}/(\text{MHP}+\text{H}_2\text{O}_2)$ ratios.

P 13097 Section 3.3. You need to provide a more compelling rational for modeling these two cases. Why not model the apparent change in MHP ratios at PKU when NO emissions were lowered? Are you only interested in the role of O_3 + alkenes as a source of CH_3OOH ? Whose radical measurements are being used to constrain the model? Are these published data? It wasn't clear to me how CH_3OO radical concentrations were inferred from the RO_x measurements. This is a very important detail.

A: There are no RO_x data available for us for Beijing 2008.

We are not just interested in ozonolysis of alkenes as a source of MHP. We are more interested in evaluating the importance of different sources and sinks in the atmospheric budget of MHP.

We have added the RO_x measurement descriptions in Section 2.3.

" HO_2 radicals were measured by a laser-induced fluorescence instrument, operated by Forschungszentrum Juelich (FZJ). Briefly, ambient air is sampled continuously into a low-pressure detection chamber, where HO_2 is chemically converted to OH by reaction with added NO. The resulting OH is then detected by laser excited fluorescence at a wavelength of 308 nm. The 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 $(1-5) \times 10^{-12}$ (volume ratio) and the systematic uncertainty was estimated to be +/-60%. Details can be found in Li et al.

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(2009).”

For the determination of CH_3O_2 , a box model with “Regional Atmospheric Chemistry Mechanism” (RACM) was employed to simulate the behavior of RO_x radicals during BG-summer 2006 and YF-summer 2006. The simulating results showed that CH_3O_2 accounted for 17% and 15% of the total RO_x radicals during noontime for these two measurements, respectively. So in this study, we use these two fractions to get the CH_3O_2 concentration from the measured RO_x concentration.

On page 13098 you infer that the MHP yield from $\text{CH}_3\text{OO} + \text{HO}_2$ must be less than 100% to match the MHP observations. This would appear to be an interesting finding. However, it seems equally plausible that you don't have an accurate measurement of CH_3OO from which to calculate a production rate. What are the uncertainties of the radical concentration measurements? This is a key problem with your analysis.

A: The accuracy of the measurements is estimated to be +/-20% and +/-60% for HO_2 and RO_x , respectively.

The absorption cross sections of CH_3OOH and H_2O_2 are different enough (factor of 2) that you should calculate the photolysis rate from the photon flux rather than just assume it is equivalent to H_2O_2 . Your removal rates for CH_3OOH are therefore in error and the MHP budget is incorrect. I'm assuming that photon fluxes were measured by someone at this site in order to calculate H_2O_2 photolysis rates. These measurements should be referenced if published.

A: Yes, we have revised this. The photo-dissociation of MHP is the least important sink compared with other two sinks, i.e., OH oxidation and deposition. The quantum yield of MHP to give CH_3O radical used in the simulation was 1.00. The absorption cross sections of MHP are lower than H_2O_2 (Data are obtained from Sander et al., 2011). MHP loss rate by photolysis recalculated are 0.0050 and 0.00026 ppbv/h for Case 1 and 2, respectively.

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P 1301. Line 1. You need to more carefully explain what the counter species are doing. For example this line states that HCHO and H₂O₂ caused conversion of NO to NO₂ but these species don't directly react with NO. So what do you mean by this. Can you give an example? This section didn't make much sense to me.

A: Yes, we added an example in the revised manuscript to explain the “Counter Species” concept:

“Let us consider the MHP chemistry in an air parcel as an example. Reactions involving the formation and removal of MHP include: (please see the reactions in the revised manuscript).

The conversion of NO to NO₂ occurs via reaction (2), (3), and (6). HO₂ radicals are produced via reaction (8), (9), and (10). So the F_s value for HO₂ radicals can be expressed as:

$$F_{HO_2} = C_3 / (C_8 + C_9 + 2 C_{10})$$

Formaldehyde cannot oxidize NO to NO₂ directly, but the photolysis and OH oxidation of formaldehyde can produce HO₂ radicals. So the F_s value for formaldehyde can be expressed as:

$$F_{HCHO} = F_{HO_2}(C_9 + 2 C_{10}) / C_8$$

Minor Concerns

P 13090 line 25. Grammar: re-word sentence “ : : : primarily subjected to S(IV) oxidation : : :” Better would be “They are important oxidants of SO₂ in cloud and rain droplets: : :”

A: Yes.

P 13090 – I would define “oxidation capacity” more carefully somewhere in the introduction. What do you mean by this: concentration of HO and O₃? See Lelieveld's 2004 paper in ACP and his paper in J. Geophys. Res. 2002 for a quantitative definition. Also

missing from your introduction is to note that CH_3OOH is a major chain termination product.

A: Yes, we have defined the “oxidation capacity” in section 3.5. Thanks for the references.

“The oxidizing capacity (oxidation power) of an air parcel is defined as the rate at which OH is produced (Lelieveld, et al., 2002 and 2004).”

P 13091: “MHP also contributes to the formation of secondary organic aerosols : : :”. While you cite the source of this information it should be explained in a general sense how MHP participates in this process – as an aqueous phase oxidant?

A: MHP contributes to the formation of water soluble organic compounds (WSOC) by dissolved into the liquid and by the subsequent photolysis to generate free radicals in the gas phase.

P 13091. Please include yields for reactions 1. A: Yes

P 13092. Please include yields for reactions 2.

A: Yes

P 13093, line 19. Typo “ : : : passes by passed by : : :”

A: We have revised the typo.

P 13093. The site experimental description could be improved. Perhaps by inclusion of a table that summarizes the important meteorological and chemical characteristics of the 4 sites. What other chemical species were measured at these sites? Were your measurements part of a larger field experiments involving other investigators? Have measurements from these sites been reported elsewhere? Were these measurements used to initialize the box model?

A: Yes, we have added a table showing meteorological conditions of the four sites and

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other measurements. Our measurement is mostly a part of field campaign organized by Peking University and other institutes. The meteorological conditions, NO_x , CO , SO_2 , NH_3 , and CH_4 concentrations used to initialize the model were representative in Beijing 2006. Publications from these campaigns include:

1. ACP - Special Issue

Program of Regional Integrated Experiments on Air Quality over the Pearl River Delta (PRIDE-PRD)

Editor(s): A. Hofzumahaus, M. Hu, S. C. Liu, and A. Wiedensohler

2. ACP - Special Issue

Regional formation processes and controlling effects of air pollution before and during the Beijing Olympics: the results of CAREBEIJING

Editor(s): D. Parrish, M. Gauss, T. Zhu, and U. Pöschl

3. JGR – Special issue

Campaigns of Air Quality Research in Beijing and Surrounding Region: 2006

Journal of Geophysical Research, vol. 115, no. D2, 2010

4. Atmospheric Acidifying Mechanism in Representative Regions (the National Basic Research Program of China).

Papers were published without special issue.

P 13096, line 1. What were the mixing ratios of SO_2 , and NO at these sites? Do you have data to show that SO_2 oxidation would be an important sink for H_2O_2 at these sites?

A: We have added a new figure (Figure 4) in the revised manuscript to show the concentration of SO_2 , NO , and CO . Our data show that there is a strong negative correlation between SO_2 and H_2O_2 .

P 13096, Line 10. Your observations of higher MHP / peroxide ratios during for the PKU 2008 measurements when NO was lower seems consistent with the Frey 2005 analysis as you cited. Could meteorology play a role in the difference – was the summer of 2008 more rainy / cloudy regionally than the other summers? Please comment.

A: It was sunny during the periods investigated (2008/07/22 – 2008/08/01). During Olympic games (2008/08/08 – 2008/08/24), most days were cloudy or rainy (during nighttime). But we did not report MHP levels during Olympic games in this study because we barely detected any signals.

P 13099 line 5. Is the MHP lifetime in winter 2-3 days? Please clarify.

A: The primary sink of MHP should be OH oxidation. So the lifetime of MHP can be simplified as:

$$\text{Lifetime} = 1 / (k[\text{OH}])$$

OH concentration in the polluted area ranges from 10^6 to 10^7 moles/cm⁻³ in the mid latitude of northern hemisphere. Since we do not have measured OH data in winter Beijing, we would use the lower limit 10^6 to represent the OH concentration in winter Beijing. Then the lifetime of MHP would be estimated as 2.9 days.

P 13100, line 16. Grammar. Remove “So” from the beginning of this sentence.

A: Yes

P 13100. Under what conditions was the model run - NO, VOCs, light levels etc. Nothing is explained to give these results context and I don't find the results very informative. Several components of figure 9 are not explained: XO₂, C₂O₃. Y-axis needs a label. A: We have added information on model constrains in Section 2.3.

We have revised figure 9. XO₂ means CH₂C(O)O and C₂O₃ means CH₃C(O)OO.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 13089, 2012.

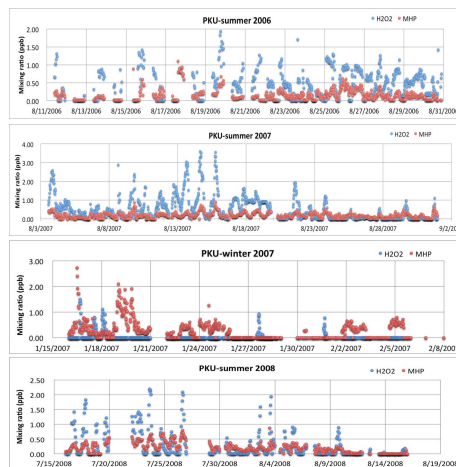
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Fig. 1. More data for H₂O₂ and MHP (1)

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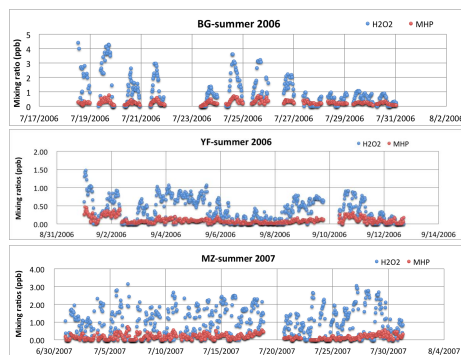
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Fig. 2. More data for H₂O₂ and MHP (2)

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