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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Methyl hydroperoxide (CH_3OOH) in urban, suburban and rural atmosphere: ambient concentration, budget, and contribution to the atmospheric oxidizing capacity" *by* X. Zhang et al.

Anonymous Referee #2

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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 measured CH3OOH mixing ratios and its impact on "oxidation capacity". The observations are of interest principally because CH3OOH measurements are infrequently reported.

The authors report that reductions in NOx 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 H2O2 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 CH3OOH photolysis rates are the same as H2O2. This means JCH3OOH 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.

Specific Concerns

P13092. 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.

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

P 13095, Section 3.1. Why are only 10 days shown and not the entire measurement period of $\sim$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

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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 NOx 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.

P 13095, Section 3.2. You need a new figure to demonstrate the statistical significance of the diurnal cycle of the peroxides (H2O2 and MHP). I suggest you plot average and median hourly values values versus time of day. I would be interested in the differences in Beijing for the 3 summers to see the influence of lower NOx in summer 2008.

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 NOx/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.

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 O3 + alkenes as a source of CH3OOH? Whose radical measurements are being used to constrain the model? Are these published data? It wasn't clear to me how CH3OO radical concentrations were inferred from the ROx measurements. This is a very important detail. On page 13098 you infer that the MHP yield from CH3OO + HO2 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 CH3OO from which to calculate a production rate. What are the uncertainties of the radical concentration measurements? This is a key problem with your nalaysis.

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The absorption cross sections of CH3OOH and H2O2 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 H2O2. Your removal rates for CH3OOH 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 H2O2 photolysis rates. These measurements should be referenced if published.

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.

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 . . ."

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 you introduction is to note that CH3OOH is a major chain termination product.

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 partipates in this process – as a aqueous phase oxidant?

P 13091. Please include yields for reactions 1.

P 13092. Please include yields for reactions 2.

P 13093, line 19. Typo " . . . passes by passed by . . ."

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Interactive Comment

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?

P 13096, line 1. What were the mixing ratios of SO2, and NO at these sites? Do you have data to show that SO2 oxidation would be an important sink for H2O2 at these sites?

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.

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

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

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.

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