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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 #1

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The paper describes CH3OOH (MHP) measurements at various urban, suburban and rural sites in China obtained during two seasons (winter and summer). Beside the discussion of the time series, diurnal variations, MHP/(MHP + H2O2) ratio, a box model is used to study the budget of MHP. Special findings are the dependency of this ratio on NOx reductions in Beijing during the Olympic Games and the transport of MHP rich air masses from the marine boundary layer towards Beijing in winter. The data itself is highly interesting and thus deserves publication in ACP. Unfortunately the data description and interpretation lacks a lot of necessary information and details that have

to be added before the paper should be accepted.

Section 2.2: This paragraph on the measurement method of MHP is rather short. In particular information on the data processing is missing. Were the MHP data corrected for the sampling efficiency? What about other organic peroxides? I assume that the HPLC also provides data on higher organic peroxides: Were any measured at significant levels? Section 2.3: MHP has a lifetime of several days. Is a box model really suitable for modeling its budget? On those timescales transport effects (vertical exchange with the free troposphere, horizontal advection) will play an important role.

Section 3.1: It would be helpful to show the H2O2 data in Figure 1.

Section 3.2: In the discussion of diurnal cycles of MHP, H2O2 and MHP/(MHP+H2O2) the effect of daytime/nighttime changes in the boundary layer height should be taken into account. Beside rainout, dry deposition processes in particular for H2O2 increase in the shallow boundary layer during the night and might thus contributesignificantly to the maximum of the MHP/(MPH+H2O2) ratio late in the night. I am also surprised that significant increases of H2O2 and MHP are only observed after noon (see Figure 3). Why is that?

In the same paragraph, the dependency of the MHP/(MHP+H2O2) ratio on NOx reductions during the Beijing Olympic games is discussed. I think one important point that the authors missed, is that the improvements in air quality will affect also other species that have an influence on the peroxide precursors. In particular, it can be assumed that reductions in NOx are associated with reductions in CO, which will affect the level of HO2 radicals, while the level of CH3O2 radicals will hardly be affected (its precursor CH4 can be assumed to be not affected by the air quality measures). Therefor reductions in CO will lead to strong reductions in the primary production of H2O2 (square dependency on HO2), while CH3OOH will be affected only marginally (linear dependency on HO2). This effect on primary production rates has to be considered in order to explain the effect of air quality measures on the ratio of peroxides.

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Interactive Comment

Section 3.3: This section on the MHP budget lacks a lot of important information. Details on the measurements of the radicals should be provided. One of the most critical aspects here is the determination of the CH3O2 radical level. How was this done based on ROx measurements?

Section 3.4: Although back trajectories indicate that the high MHP levels were associated with marine boundary layer air, I find it very disturbing that those air masses have nearly zero H2O2. You would expect that the marine boundary layer contains rather high levels of H2O2 (similar to MHP). What happened to the H2O2? Are there indications for cloud processing/rain-out that might explain the complete removal of H2O2?

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