

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.

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 NO_x 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

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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 contribute significantly to the maximum of the MHP/(MHP+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 NO_x 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 NO_x 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). Therefore 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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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 RO_x 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?

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