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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.

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The paper describes CH_3OOH (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 + H_2O_2) 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 to be added before the paper should be accepted.

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.

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?

A: We have added more descriptions on Section 2.2.

The collection efficiency is 85% for MHP and 100% for H_2O_2 at a scrubbing coil temperature of 10 °C. The scrubbing coil temperature was controlled at 10 °C for BG-and summer 2006 and 4 °C for other observations. All the published data have not been corrected by the sampling efficiency because we think that this collection efficiency is enough high for the field measurement. The method we used to determine the collection efficiency is as follows: First, vapor containing MHP was generated by a saturated vapor generator. The air stream with 100% RH flowed over the thermostatically controlled quartz fiber membrane (15 °C), which was saturated by the standard solution, at a rate of 0.2 slm. Second, additional pure air (2.5 slm) was added to the generated vapor of MHP via a three-port valve. Then the mixed air stream of standard gas MHP was drawn into the scrubbing coil collector at a total flow rate of 2.7 slm under the conditions used for atmospheric measurement. Using a solution containing 3.5×10^{-6} M MHP, the levels of gaseous MHP in the standard gas were calculated to be 0.5 ppbv. The concentration of this standard gas was also determined using a Horibe tube in a cold trap of ethanol/liquid nitrogen at $-$ 90 °C for collection and for HPLC analysis. The collection efficiency of the coil was estimated using the ratio of the measured concentration and the known concentration of the standard gas. The heterogeneous decomposition of MHP in the coil was negligible under the experimental conditions. The collection efficiency of H_2O_2 was determined by the same method using a concentration of 1 ppbv.

The measurement procedure has been published in our previous studies (Hua et al., 2008; Zhang et al., 2010). Our HPLC method can now mainly detect H_2O_2, MHP, and PAA (peroxyacetic acid). During these seven measurements, PAA was usually present in tens of pptv level.

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.

A: Yes, we agree with the reviewer. For investigating the budget of MHP in Section 3.3, we focus on several hours' chemical kinetics. According to the second reviewer's suggestion, we have deleted the influence of MHP on free radicals budget. We would like to keep Section 3.5 (Contribution of MHP to the atmospheric oxidizing capacity) in the revised draft. We thought it is important and necessary to know the oxidizing power of MHP in an air parcel, which is assumed to have no physical exchange with environment. In this way, we can simplify the treatment of diffusion and transportation and to represent chemical mechanisms in great detail.

Section 3.1: It would be helpful to show the H_2O_2 data in Figure 1.

A:Yes. We have added H_2O_2 data in Figure 1.

Section 3.2: In the discussion of diurnal cycles of MHP, H_2O_2 and MHP/(MHP+H_2O_2) the effect of daytime/nighttime changes in the boundary layer height should be taken into account. Beside rainout, dry deposition processes in particular for H_2O_2 increase in the shallow boundary layer during the night and might thus contribute significantly to the maximum of the MHP/(MPH+H_2O_2) ratio late in the night. I am also surprised that

significant increases of H_2O_2 and MHP are only observed after noon (see Figure 3). Why is that?

A: We agree with the reviewer. Thanks for the constructive suggestions. We revised this section, also including answers to reviewer's questions, as shown below:

"……A typical diurnal variation of MHP/(MHP+H_2O_2) ratio in PKU-summer 2008 is shown in Fig. 3, together with corresponding H_2O_2 and MHP mixing ratios. The diurnal profile of MHP is consistent with that of H_2O_2 during daytime, which can be explained by vertical mixing and local photochemical production in a sunlit day. From sunrise, the photochemical production initiated and MHP concentration started to rise, reaching a maximum level at 14:00 LT. Its level remained relatively high in the late afternoon and sometimes a shoulder peak was observed around 17:00 LT, which can be attributed to the secondary emission of pollutants during traffic hours. The MHP/(MHP+H_2O_2) ratio, however, was out phase with H_2O_2 and MHP mixing ratios, peaking during the night and early morning (0:00 – 6:00) and decaying rapidly in the afternoon (15:00 – 19:00). The high values in the night and early morning indicate a preferential depletion of H_2O_2 to MHP. The shallow boundary layer height accelerates the dry deposition processes in particular for H_2O_2 during night, resulting in a substantial decease in H_2O_2 concentration. In addition, the high relative humidity (RH) during nighttime accelerates two H_2O_2 removal pathways: deposition to water droplets and aqueous-phase oxidation of S(IV), both of which are much less important for MHP. "

In the same paragraph, the dependency of the MHP/(MHP+H_2O_2) 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 HO_2 radicals, while the level of CH_3O_2 radicals will hardly be affected (its precursor CH_4 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 H_2O_2 (square dependency on HO_2), while CH_3OOH will be affected only marginally (linear dependency on HO_2). 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.

A: Yes, we did miss this important issue. During the period investigated, the average CO concentration was 1.28 ppmv in 2007 and 1.00 ppmv in 2008, respectively. To evaluate the effect of NO on the MHP/(MHP+H_2O_2) ratio, we also investigated two daily basis measurements, which were carried out on 08/15/2007 and 07/23/2008. The revised paragraph is shown as follows:

"…The primary difference is that a full scale control of atmospheric pollutants was implemented to improve the air quality prior to the 2008 Beijing Olympic Games, resulting in a significant decrease in the emission of pollutants, such as NO_x, CO, and SO_2, in urban Beijing (Wang et al., 2009). Note that the dependency of the MHP/(MHP+H_2O_2) on the NO_x level change might be overestimated here because of the interference of CO reduction, which leads to a decrease in HO_2 radical concentration. Assuming the level of CH_3O_2 radical remains constant, reductions in CO will result in strong decrease in the primary production of H_2O_2, whereas MHP will be affected only marginally. In view of this effect, we also presented here two daily basis measurements, which were carried out on August 15 2007 and July 23 2008, respectively. The CO concentrations, together with the meteorology conditions were consistent for these two periods investigated, whereas the NO concentration on 08/15/2007 was substantially higher. As a result, the MHP/(H_2O_2+MHP) ratio was much lower in the presence of high level of NO_x, as shown in Fig. 4. ..."

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 CH_3O_2 radical level. How was this done based on RO_x measurements?

A: Yes, we have added measurement methods for RO_x in Section 2, also shown below:

"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. (2009)."

For the determination of CH_3O_2, a box model incorporated 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.

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 H_2O_2. You would expect that the marine boundary layer contains rather high levels of H_2O_2 (similar to MHP). What happened to the H_2O_2? Are there indications for cloud processing/rain-out that might explain the complete removal of H_2O_2?

A: The meteorological data shows that there was no precipitation during the period investigated at PKU site. It is possible that there were precipitations on the way of air masses from the ocean to the observational site. The height of back trajectories simulated is 500 m, where cloud processing can be neglected.

We also found that there is a strong negative correlation between H_2O_2 and SO_2 whereas the relationship between MHP and SO_2 is less obvious. This suggests a preferential depletion of H_2O_2 by the aqueous phase reaction with SO_2. On Jan 19 2007, the average RH was 45.3% and the SO_2 concentration was consistently high. This might be one important reason to explain what happened to H_2O_2.

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