

## ***Interactive comment on “Peroxyacetic acid in urban and rural atmosphere: concentration, feedback on PAN–NO<sub>x</sub> cycle and implication on radical chemistry” by X. Zhang et al.***

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Received and published: 6 January 2010

Response to Prof. D Möller (Reviewer 2)

Thanks for your effort and constructive comments. Here are our responses to your comments:

(Q1) General Comments: This paper is to my knowledge the first in literature with a comprehensive data set on PAA and related parameters to analyse the atmospheric chemistry of PAA. It is therefore welcome in the atmospheric chemistry community. It is well written with a clear description of the measurement sites and analytical procedures. It is known that all organic peroxides have a competition to H<sub>2</sub>O<sub>2</sub> formation

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and it is therefore important to model the different formation pathways correctly for a better description of the oxidation potential. It seems from the finding of this paper that PAA has a close (and reliable) relation to PAN which makes it special in comparison to other organic peroxides. However, there is a fundamental difference between the origin of H<sub>2</sub>O<sub>2</sub> and all organic peroxides: the latter need organics for its direct formation and H<sub>2</sub>O<sub>2</sub> is only very weak or indirectly depending from VOCs. This aspect is not so clear expressed in the discussion of the result by Zhang et al. Unfortunately, no VOC measurements are obviously available from the measurement sites to look for the PAA (and MHP) to VOC correlation without modeling. Moreover, and that is an important point, it seems that MHP (as the most simple organic peroxide) should have a strong correlation with VOCs whereas PAA not but to PAN.

(A1) We highly appreciate Prof. Möller for your comments and suggestions. As you pointed out, the formation of organic peroxides depends directly on the varieties and levels of VOCs in the atmosphere. Particularly speaking, only the photochemical oxidation of some specific VOCs can produce CH<sub>3</sub>OO and CH<sub>3</sub>C(O)OO, which are precursors of MHP and PAA. So it is necessary to explore the relationship between VOCs and organic peroxides using observational data. Unfortunately, we could not clearly express this relationship in the present study because some on-line VOCs data are not available to us now. Anyway, you have put forward a very interesting and important topic, which we will work on in the future.

(Q2) To the general observation: In 2007 at two sites, Beijing and Mazhang daytime and nocturnal PAA concentrations are surprisingly large. While proposing that the UV-B radiation was by a factor 2-3 higher than in the other periods, the authors conclude on photochemical activity. Generally this is true. Is the same found for H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>? Or were there different air masses with different air chemical history?

(A2) After comparing peroxides and ozone data among these five campaigns, we think the average levels of ozone and peroxides in Beijing 2007 and Mazhuang 2007 were actually higher than those in other places. For ozone, we have randomly chosen five

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days from each measurement and its concentrations are shown in the following Fig. 1. Although the maximum value occurred in Beijing 2008, the average concentrations at Mazhuang 2007 and Beijing 2007 were obviously higher.

For H<sub>2</sub>O<sub>2</sub>, the average concentrations in Beijing 2006, Beijing 2007, Beijing 2008, Backgarden 2006, and Mazhuang 2007 were 0.53 ppbv, 0.65 ppbv, 0.27 ppbv, 1.00 ppbv, and 0.95 ppbv, respectively. It should be noted that in Beijing 2006 and Backgarden 2006, peroxides data at night (00:00 – 06:00) were scarce because samples were injected manually into the HPLC valve at that time, resulting in the overestimated average concentrations of H<sub>2</sub>O<sub>2</sub> in these two measurements.

#### Meteorological and chemical factors

(Q3) It seems to me that many authors overestimate the local (in-situ) photochemical production of any secondary compounds such as peroxides, ozone etc. In Möller (2004, 2009) it was clearly shown that vertical mixing (downward transport from the residual layer after having a nocturnal inversion layer what is common for “sunny” summer days) is the dominant contributor to the increase of these compounds after sun set. Additionally local photochemistry (or generally speaking boundary layer photochemistry and advective transport) starts and further increase the concentration (of PAA, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>), resulting in a shift of the maximum later than the meteorological midday. Because O<sub>3</sub> is the precursor (for OH/HO<sub>2</sub> photochemical production) for H<sub>2</sub>O<sub>2</sub>, all three oxidants depend from VOC degradation what is a relatively slow process which needs time (hours to days) depending from the VOC split according to the specific VOC reactivity to OH.

(A3) Yes, we have rewritten the paragraph about PAA temporal variation, as follows: “The time series of PAA, H<sub>2</sub>O<sub>2</sub> and MHP on 2 Aug 2008, a sunny day in Beijing, were shown in Fig. 3. The diurnal profile of PAA was similar to those of H<sub>2</sub>O<sub>2</sub> and MHP. This can be explained by vertical mixing and local photochemical production in a sunlit day (Möller et al., 2004, 2009). From sunrise, the inversion layer was broken and PAA was

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transported down by vertical mixing. The photochemical reactions began later and consequently, PAA concentration started to rise, reaching a maximum level at 17:00 LT. Its level remained relatively high in the late afternoon and decayed rapidly due to the dry deposition from the sunset to 24:00 LT. Throughout the night, there seemed to be no obvious transportation from the residual layer to the surface layer and PAA was depleted even to zero till the early morning.”

#### References:

Möller, D.: The tropospheric ozone problem, *Archives of Industrial Hygiene and Toxicology*, 55, 11 - 23, 2004.

Möller, D.: Atmospheric hydrogen peroxide: evidence for aqueous-phase formation from an historic perspective and a one-year measurement campaign, *Atmos. Environ.*, 43, 5923 - 5936, 2009.

(Q4) The inverse correlation between PAA (and all other peroxides) with NO<sub>x</sub> is evident (and simple to explain) and has been often shown in literature. The (inverse) correlation with SO<sub>2</sub> however is somewhat more complex. Peroxides are consumed only in the aqueous phase, i.e. in droplets. It is also possible that at the surface of activated CCN having an aqueous layer, peroxides can be scavenged (together with SO<sub>2</sub>) and hence consumed. But it is very likely that this removal flux is very limited (unfortunately there is no model what can describe this process) due to several reasons, for example limited surface in the air volume, saturation of the particle water layer, strong surface acidification and other. The data shown suggest RH to be far from particle activation; moreover there was no rain or fog. Therefore we can assume that there was no aqueous phase peroxide consumption.

(A4) It is true that the consumption of PAA by oxidizing SO<sub>2</sub> in the aqueous phase was to be minus in a sunny day. We have deleted the related discussion about the anti-correlation between SO<sub>2</sub> and PAA.

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(Q5) The “correlation” between SO<sub>2</sub> and PAA therefore should have other causes (e.g. different sources such as local emission, transport etc.). It is right that peroxide have a large dry deposition velocity (the surface resistance can be set to be zero). Hence, any structured surface like forest increase to dry deposition flux. However in the “free troposphere” (page 22590 line 27) no dry deposition flux can be established.

(A5) Yes, we have revised this sentence.

(Q6) From Fig. 3 it seems that the “correlation” between PAA and H<sub>2</sub>O<sub>2</sub> is excellent but not to MHP. The authors conclude from Fig. 8 a weak correlation between PAA and H<sub>2</sub>O<sub>2</sub> (and further discuss the H<sub>2</sub>O<sub>2</sub> removal likely in the early morning). With the exception of the time 02:00 to 07:00 I see a better correlation between PAA and H<sub>2</sub>O<sub>2</sub> than found from Fig. 3. As already mentioned, MHP formation strongly depends from reactive VOCs. It would be interesting to discuss the reason why MHP was so small on 2 August 2008 in Beijing comparing to PAA and H<sub>2</sub>O<sub>2</sub>. On the other hand, PAA and MHP are very close at Mazhuang on 6 July 2007 (also to H<sub>2</sub>O<sub>2</sub> which still show a higher concentration). My feeling is that the main process of (photochemical) formation occurs in the whole boundary layer and lower free troposphere. In the case of no precipitation (and all data from the measurement campaigns suggest it) there is an accumulation of the peroxide in air. Reservoir distribution between surface layer and more upper layer depends from transport characteristics. This includes of course the build-up of the nocturnal inversion layer with the depletion of peroxide at ground.

(A6) Actually, the concentration of MHP was not so small. The maximum values of H<sub>2</sub>O<sub>2</sub>, MHP, and PAA were 1.76 ppbv, 0.54 ppbv, and 0.091 ppbv on 2 Aug in Beijing. The concentration scale in Fig. 3 in the previous manuscript for PAA (the right Y-axis) was different from that for H<sub>2</sub>O<sub>2</sub> and MHP (the left Y-axis). If Fig. 3 did not include H<sub>2</sub>O<sub>2</sub>, it would better show the temporal profiles of MHP, see the following Fig. 2. We have redrawn Fig. 3 in the revised manuscript, adjusting the scale for MHP.

As for the transport of H<sub>2</sub>O<sub>2</sub> from upper atmosphere, we agree with you that it is a

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possible source of H<sub>2</sub>O<sub>2</sub> at night. Actually, several studies have reported the downward transport of H<sub>2</sub>O<sub>2</sub> (Takami et al., 2003; Ganzeveld, et al., 2006). We have added some related discussions in the Section 3.3.3. in the revised manuscript.

References:

Ganzeveld, L., Valverde-Canossa, J., Moortgat, G. K., and Steinbrecher, R.: Evaluation of peroxide exchanges over a coniferous forest in a single-column chemistry-climate model, *Atmos. Environ.* 40, S68 - S80, 2006.

Takami, A., Shiratori, N., Yonekura, H., and Hatakeyama, S.: Measurement of hydroperoxides and ozone in Oku-Nikko area, *Atmos. Environ.*, 37, 3861 - 3872, 2003.

(Q7) I am wondering why some compounds show such strong fluctuation between the sampling (analytical) data (Figs. 3, 5, 7 and 9). It would be interesting to discuss the reason why all peroxides go down to zero at Mazhuang on 17:00 and rise again significant in the evening. Why SO<sub>2</sub> shows three spikes? When there are no technical problems, the only explanation to me is air mass fluctuation. This can be discussed with (possibly) available meteorological values.

(A7) Thanks for your suggestions. It is true that the possible reason was air mass fluctuation. Figure 3 shows the temporal profiles of other pollutants on 6 July at Mazhuang (The data of wind direction and speed was not available on that day). It is clear that at around 12:00, an air-mass transported to the sampling inlet, resulting in the increase of SO<sub>2</sub> and NO<sub>x</sub>, and the decrease of ozone and all the peroxides. However, from 17:00 to 19:00, only SO<sub>2</sub> and the three peroxides exhibited strong anti-correlation. We have added some discussions in Section 3.3.3 in the revised manuscript.

(Q8) On page 22596 line 6 the authors suggest that sinks of H<sub>2</sub>O<sub>2</sub> were potentially different from those of MHP and PAA. To me, Fig. 8 shows no strong correlation (but a correlation) between PAA and MHP, suggesting the common formation pathway via VOCs. Beside the argument of different sinks also different sources may be discussed:

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the concentration at a given site reflects always a budget between sinks and sources. Ozonolysis could be a source of H<sub>2</sub>O<sub>2</sub> (in case of high humidity directly to H<sub>2</sub>O<sub>2</sub> otherwise primarily to HO<sub>2</sub>/OH). However we did observe also during night spikes in H<sub>2</sub>O<sub>2</sub> (we never studied organic peroxides specifically) and contribute that phenomenon to short-time vertical mixing processes from the free troposphere (evidence we found by sodar sounding). Again it is important that under some conditions the formation process of H<sub>2</sub>O<sub>2</sub> (see also in Möller 2009) could be different from those of MHP and PAA.

(A8) As far as we know, there are three H<sub>2</sub>O<sub>2</sub> production pathways in the gas phase at night: (1) the ozonolysis of alkenes in the presence of water vapor (Becker et al., 1993; Sauer et al., 1999; Hasson et al., 2003); (2) the nighttime reactions of NO<sub>3</sub> with aldehydes and alkanes, which could produce RO<sub>x</sub> and HO<sub>x</sub> radicals (Wayne et al., 1991; Atkinson 1991), thus contributing to the night production of H<sub>2</sub>O<sub>2</sub> and organic peroxides; and (3) the subsidence of H<sub>2</sub>O<sub>2</sub> from aloft where chemical production occurs (Takami et al., 2003; Ganzeveld, et al., 2006). In addition, other sources, like combustion (e.g. biomass burning) and aqueous formation will possibly contribute to the H<sub>2</sub>O<sub>2</sub> formation (Möller et al., 2009).

We have rewritten Section 3.3.3, including discussing the possible sources of peroxides, in the revised manuscript.

References:

Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the NO<sub>3</sub> radical with organic compounds, *J. Phys. Chem. Ref. Data*, 20(3), 459-507, 1991.

Becker, K. -H., Brockmann, K. J., and Bechara, J.: Production of hydrogen peroxide in forest air by reaction of ozone with terpenes, *Nature*, 346, 256 - 258, 1990.

Möller, D.: Atmospheric hydrogen peroxide: evidence for aqueous-phase formation from an historic perspective and a one-year measurement campaign, *Atmos. Environ.*, 43, 5923 - 5936, 2009.

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Sauer, F., Schäfer, C., Neeb, P., Horie, O., and Moortgat, G. K.: Formation of hydrogen peroxides in the ozonolysis of isoprene and simple alkenes under humid conditions, *Atmos. Environ.*, 33(2), 229-241, 1999.

Wayne, R. P., Barnes, I., Biggs, P., Burrows, J. P., Canosa-Mas, C. E., Hjorth, J., Le Bras, G., Moortgat, G. K., Pertner, D., Poulet, G., Restelli, G., and Sidebottom, H.: The nitrate radical: physics, chemistry, and the atmosphere, *Atmos. Environ.*, 25A(1), 1-203, 1991.

(Q9) Final comment Finally the Zhang et al. paper is a very important contribution to the peroxide chemistry. It is never possible to include all parameters which would be necessary for interpreting the results into campaigns before having the results. It is strongly emphasized to continue selected campaigns in this direction.

(A9) We highly appreciate your final comments.

Technical Comments:

(Q10) On page 22585 line 9 "Silicon Valley" should given in parenthesis. I know and like this area but there is no link to Silicon Valley.

(A10) Yes, we have revised that.

(Q11) The Figures are so small that the reader needs a magnifier.

(A11) We have magnified some of them.

(Q12) The analytical expressions concerning PAN may be omitted and this paragraph can be a little condensed.

(A12) Yes, we have deleted relevant expressions.

(Q13) On Fig. 4 at least one time should be marked (I assume that the dotted line is 24:00 of July 20).

(A13) Yes, we have redrawn this figure.

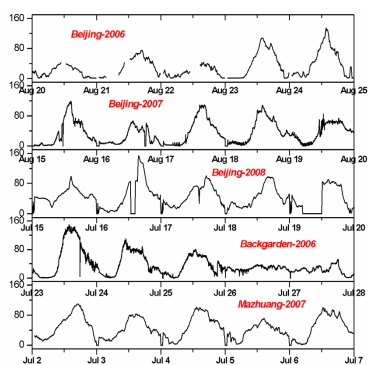
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(Q14) The subparagraph in 3.3.3 on aqueous phase reactions should be omitted because all evidence is that during the campaigns there was no aqueous phase chemistry.

(A14) Yes, we have rewritten this section, omitting the discussion about aqueous phase chemistry.

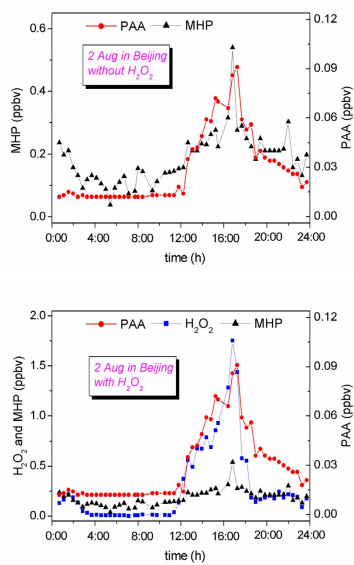
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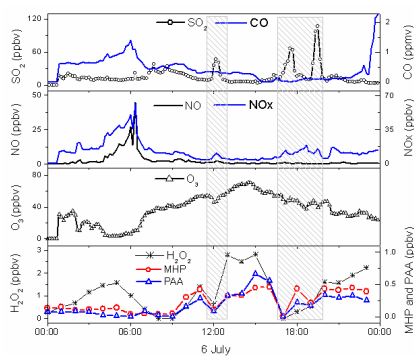
**Fig. 1.** Temporal profiles of atmospheric ozone concentrations during five campaigns.

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**Fig. 2.** Temporal profiles of H<sub>2</sub>O<sub>2</sub>, MHP, and PAA on 2 Aug in Beijing

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**Fig. 3.** Diurnal variations of PAA, H<sub>2</sub>O<sub>2</sub>, MHP, and primary pollutants at Mazhuang on 6 July 2007.

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