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Atmospheric
Chemistry
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Discussions

Interactive comment on "Peroxyacetic acid in urban and rural atmosphere: concentration, feedback on PAN$-$NO$_x$ cycle and implication on radical chemistry" *by* X. Zhang et al.

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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 H2O2 formation 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 H2O2 and all organic peroxides: the latter need organics for its direct formation and H2O2 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 modelling. 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.

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 H2O2 and O3? Or were there different air masses with different air chemical history?

Meteorological and chemical factors

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, H2O2 and O3), resulting in a shift of the maximum later than the meteorological midday. Because O3 is the precursor (for OH/HO2 photochemical production) for H2O2, 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.

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Interactive Discussion

Discussion Paper

The inverse correlation between PAA (and all other peroxides) with NOx is evident (and simple to explain) and has been often shown in literature. The (inverse) correlation with SO2 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 SO2) 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.

The "correlation" between SO2 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.

From Fig. 3 it seems that the "correlation" between PAA and H2O2 is excellent but not to MHP. The authors conclude from Fig. 8 a weak correlation between PAA and H2O2 (and further discuss the H2O2 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 H2O2 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 H2O2. On the other hand, PAA and MHP are very close at Mazhuang on 6 July 2007 (also to H2O2 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.

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 SO2 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.

On page 22596 line 6 the authors suggest that sinks of H2O2 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: the concentration at a given site reflects always a budget between sinks *and* sources. Ozonolysis could be a source of H2O2 (in case of high humidity directly to H2O2 otherwise primarily to OH2/OH). However we did observe also during night spikes in H2O2 (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 H2O2 (see also in Möller 2009) could be different from those of MHP and PAA.

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.

Technical Comments:

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*. The Figures are so small that the reader needs a magnifier. The analytical expressions concerning PAN may be omitted and this paragraph can be a little condensed. On Fig. 4 at least one time should be marked (I assume that the dotted line is 24:00 of July 20). 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.

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Möller, D. (2009) Atmospheric Hydrogen Peroxide: Evidence for aqueous-phase formation from an historic perspective and a one-year measurement campaign. Atmos. Environ. 43, 5923-5936

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22581, 2009.