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# *Interactive comment on* "Impacts of aerosols on the chemistry of atmospheric trace gases: a case study of peroxides and $HO_2$ radicals" *by* H. Liang et al.

**Anonymous Referee #2**

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In this paper Liang et al attempt to use field measurements of peroxides (in particular H2O2) in combination with observations of aerosols during non-haze and haze conditions in Beijing to further understand the aqueous phase chemistry of HO2 and H2O2, and to determine whether H2O2 is re-released from the aerosol following the uptake of HO2. There is some controversy in the literature regarding the fate of HO2 following uptake onto an aerosol that contains transition metal ions (TMI). The traditional argument is that following uptake HO2 reacts with its conjugate base O2- to form H2O2, in a process that is catalysed by TMI, in particular copper, which is then released back to the gas phase being partitioned according to the Henry's Law constant. A more recent argument by Mao et al is that with mixtures of Fe/Cu a different mechanism following HO2 uptake generates H2O rather than H2O2. This has important implications for the HOx budget, as aerosol processing of HO2 in the past provides a source of H2O2 back into the gas phase, and so is not a sink for HOx, whereas the formation of H2O switches off the production of H2O2 and hence the source of HOx and modelled HOx is lower. Previous field campaigns have shown that the switching off of the H2O2 formation in the aerosol can help to bring modelled HOx into better agreement with field measurements (e.g., during ARCTAS). In this work CH3C(O)OOH is also measured (PAA) in the gas phase, which is a product of aqueous chemistry of organic peroxy radicals (as well as being formed in the gas phase fro RO2+HO2), and may help to elucidate further the aerosol processing of peroxy radicals. A model based on the MCM and constrained by measurements of NOx, O3, aerosol parameters etc (including liquid water content which allows identification of whether the aerosols are aqueous allowing the solution chemistry to occur, or dry in which case not), and including an aqueous scheme from CAPRAM, and extended using the scheme of Mao et al., is used to try to reproduce the measurements of H2O2 and other peroxides under various loadings of organic aerosols. The novel aspect here is magnitude of the potential aerosol sink for HO2 and H2O2, which can be very large during haze events.

Anticorrelations between H2O2 and PAA suggest that H2O2 may be converted to PAA in solution. The standard model was able to reproduce H2O2 on non-haze days, but when the loading of aerosols was very high, the model significantly overpredicts H2O2. The modelled H2O2 is lowered and in better agreement with measured H2O2 if the newly proposed TMI scheme of Mao is included, which generates H2O and not H2O2, and so H2O2 is not released to the gas phase lowering the modelled H2O2. Under rainwater conditions the model underpredicts H2O2 if the aqueous chemistry of HO2 with O2- is not included (providing evidence that this reaction is occurring).

This is a good paper which does help to partly support novel aqueous chemistry taking place. However, the results are by no means clear-cut, and some of the parameters used in the model have considerable uncertaintly. For example there are no VOC measurements and so average values from 2007 are used, which must introduce considerable uncertainty. Owing to this too much discussion of the absolute levels of H2O2 calculated probably is not appropriate, and the focus should be on the difference when the various aqueous schemes are switched on and off. Also, without field measurements of OH and HO2, which would have provided a very important model target, it is difficult to know whether the improved model agreement for H2O2 is due to the uptake of HO2 but without recycling of H2O2 to the gas phase, or some other impacts on H2O2, for example direct uptake or deposition, or changes in the photolysis frequency, which varies considerably between haze and non-haze events. The model is not that well constrained – VOCs were not measured, as other parameters, such as the concentration of HOx, had to be assumed, and although a sensitivity analysis is performed to show the impact of not knowing these parameters well for the prediction of H2O2, there is quite a bit of uncertainty. The reviewer strongly agrees that further laboratory studies of the heterogeneous chemistry of H2O2 and HO2 are needed in order to understand the budget of the important species H2O2 in the atmosphere.

The paper is suitable for publication in ACP, but the authors should consider the above and the points made below.

There are some more recent papers on lab studies of the uptake of HO2 onto aerosols, for example Taketani et al., George et al and Thornton et al., which should be referenced. It should be noted that there is some considerable discrepancy in the values of the uptake coefficient for HO2 onto aerosols.

Some more quality control/quality assurance details should be given regarding the technique used to measure H2O2, MHP and PAA. What is the uncertainty in the measurements for example, and has the technique been intercompared with other methods to gauge its reliability and accuracy? Section 2.3 – title inadequate, “others?”

Section 2.4.2. Line 18, it is stated that the mass accommodation coefficient used

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is unity. This is not the experimentally measured value for HO2 – which has been determined as around 0.5, i.e. a factor of 2 lower (see Taketani et al., George et al., Thornton et al.). What is the impact of using unity rather than the true value?

What sort of correction does the Mao et al scheme make for the bulk HO2 concentration compared to its surface concentration (line 25)? Is there evidence that the bulk and surface will change significantly?

Page 16560, line 12 "intensively" is not really the right word "significantly" or "rapidly" is better.

How accurate is the calculation of photolysis frequencies using TUV , under hazy, cloudy conditions one might imagine that this could be significantly in error. This is important in order to rule out that the reduction of H2O2 during the haze periods is due to aerosols rather than changes in radiation. More discussion of this point and the likely accuracy of J values, and some discussion of the sensitivity of the H2O2 concentration in the model to this parameter is needed (it is not one of the factors changed in Table 3). The authors do "tentatively" ascribe the lower H2O2 due to aerosols, suggesting that there is some considerable uncertainty whether this is the case or not. The PO/O3 ratio is a good point to make in support of heterogeneous processes being important

Page 16565, line 1, replace "diversity" by "variability".

I found the description of the model a little incomplete. The model did not simulate MHP and PAA well – is this because of the lack of VOC measurements which are the original source of the organic peroxides? The real problem is the lack of VOC measurements to constrain the model. I would like to see a more detailed discussion of the implications of using the 2007 VOC average data. Is there evidence of year to year variability, or in deed variability in VOC levels between non-haze and haze events? VOCs will be the major sink for OH in this environment (evidence from measurements of OH reactivity and comparison with modelled values, e.g. for Beijing), and as OH/HO2/H2O2 are so closely coupled, the absence of VOC measurements must represent a serious

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limitation on being able to model $H_2O_2$. The sensitivity analysis does provide some indication of the impact of changing certain VOCs in the modelled $HO_x$ and $H_2O_2$, but it does not indicate how a change in the mix of VOCs or errors in the assumed distribution of different types of VOCs may influence the results.

Page 16568 line 21. Which processes are not included in the present study, the Mao et al processes or uptake on solid surfaces, I think the later but this should be made clear.

Page 16569 – I found this section long and hard to follow. Please tighten up the text and make clearer.

Is there any direct evidence on whether the aerosols present are aqueous or dry?

Page 16572, line 21. Uptake coefficients of $HO_2$ of 0.86 is used for non-haze days and 0.68 on haze days. These values seem too high. Even the mass accommodation coefficients for $HO_2$ (measured using copper doped aerosols) are of the order of 0.4-0.5. So I think the fact that the model needs these very high values in order to make the $H_2O_2$ match with the field measurements suggests that something else must be going on. The authors should acknowledge that the values they quote here are too high given the experimental database.

Section 4, summary. Page 16573, line 16 – quantify what "much lower peroxide levels" means, give a numerical value. Same comment about the seemingly unreasonably high uptake coefficients for $HO_2$ that are needed to get closure on the model for $H_2O_2$ and $HO_2$.

Figures. General point is that error bars are needed on all plots where peroxide and other concentrations are compared for haze and non-haze days (Fig 6), and when $H_2O_2$ is compared with the model. Model and measurement error bars should be shown so that the level of agreement and any discussion of this can be critically evaluated.

Figure 9 – it is hard to see the numbers with the coloured background. Suggest removing the colour on the background and just lave the bubbles, arrows, and values next to the arrows.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 16549, 2013.