Atmospheric
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Discussions

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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.

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Thanks for your constructive and thoughtful comments. We have revised our manuscript, according to your comments. Below is our response, as shown in answer (A), to your comments.

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 uncertainty. For example there are no VOC measurements and so average values from 2007 are used, which must introduce con-

siderable uncertainty. Owing to this too much discussion of the absolute levels of H$_2$O$_2$ 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 HO$_2$, which would have provided a very important model target, it is difficult to know whether the improved model agreement for H$_2$O$_2$ is due to the uptake of HO$_2$ but without recycling of H$_2$O$_2$ to the gas phase, or some other impacts on H$_2$O$_2$, 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 HO$_x$, 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 H$_2$O$_2$, there is quite a bit of uncertainty. The reviewer strongly agrees that further laboratory studies of the heterogeneous chemistry of H$_2$O$_2$ and HO$_2$ are needed in order to understand the budget of the important species H$_2$O$_2$ in the atmosphere.

A: We agree with you that the lack of VOCs and HO$_x$ measurement brings considerable uncertainties to the modeling results. In the revised manuscript, we have provided more evaluations and sensitivity analyses as per your suggestions in order to minimize these uncertainties.

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 HO$_2$ 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 HO$_2$ onto aerosols.

A: We agree. We have added the statement and also references in the introduction as: "A number of laboratory studies revealed that the aerosols could greatly take up HO$_2$ radicals, although the values have considerable discrepancy, ranging from <0.01

to 0.40, depending on the components of the particles and experimental conditions (e.g., Bedjanian et al., 2005, 2013; Thornton and Abbatt, 2005; Taketani et al., 2008, 2009, 2010, 2012; George et al., 2013)."

Some more quality control/quality assurance details should be given regarding the technique used to measure H_2O_2, 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?

A: This is an important question. The measurement method has not been compared with other methods in the present study. In addition to the method of HPLC with derivation fluorescence, there is a CIMS (Chemical Ionization Mass Spectrometry) method (e.g., Crounse et al., 2006; Phillips et al., 2013). Unfortunately, we did not compare our HPLC method with CIMS because it was unavailable in China. Our method was carefully evaluated in both literature (e.g. Sauer et al., 1996, 2001) and our previous study (Hua et al., 2008). The heterogeneous decomposition and the artifact production of peroxides in the tubing were negligible. The multipoint calibration showed that the peroxide presented a good linear response in a wide concentration range relative to the atmosphere. In the field, single point calibrations were performed twice a day with a mixing standard solution. The largest uncertainty came from the interference of SO_2. H_2O_2 concentrations were underestimated by ∼10%, ∼30% and ∼50% when SO_2 concentrations were 10, 20, 50 ppbv (parts per billion by volume), respectively. The average concentrations of SO_2 were determined to be 4.0±2.6 ppbv in August 2010 and 2.1±1.7 ppbv in August 2011, indicating that the H_2O_2 loss caused by SO_2 interference was typically less than 10% during our measurements. The loss of organic peroxides caused by SO_2 interference was smaller than that of H_2O_2. Therefore, our observational data for the peroxides were reliable. Further details on this method can be found in Hua et al. (2008). We have added the above statement in the revised manuscript.

Section 2.3 – title inadequate, "others?"

A: Yes, we have changed the title of Section 2.3 from "Measurement method for others" to "Measurement method for other trace gases and meteorological parameters".

Section 2.4.2. Line 18, it is stated that the mass accommodation coefficient used is unity. This is not the experimentally measured value for HO_2 – 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?

A: That is a great question. When the α_{HO2} is changed from 1 to 0.5 in the model, HO_2 and H_2O_2 concentrations decrease only by 0.3% and 4.0%, respectively, although both the uptake and volatilization rate constants (k_{in} and k_{out}) are reduced by up to 50%. Thornton and Abbatt (2005) suggested that the experimentally measured α_{HO2} was sometimes showing the lower limit owing to diffusion limitations and for aqueous aerosols α_{HO2} was likely to be near unity. We used unity as the α_{HO2} value in the present study.

What sort of correction does the Mao et al scheme make for the bulk HO_2 concentration compared to its surface concentration (line 25)? Is there evidence that the bulk and surface will change significantly?

A: Mao et al. used the equation from Jacob (1986) to express the relationship between bulk and surface concentration of HO_2. The equation is as follows:

$$[HO_2]_{sulf} = \frac{P_{HO_2}}{k^I} + \left([HO_2]_{bulk} - \frac{P_{HO_2}}{k^I}\right) \left[3\left(\frac{cothq}{q} - \frac{1}{q^2}\right)\right]^{-1}$$

where kI is the first-order loss constant of HO_2, P_{HO2} is the aqueous-phase production rate of HO_2, and

$$q = r\left(k^I/D_{aq}\right)^{1/2}$$

is the diffuso-reactive parameter, in which r is the radius of the particles, and D_{aq} is the HO_2 aqueous phase diffusion constant. According to this correction, the surface concentration is 100% to 180% of the bulk concentration, depending on the radius

of the particles and the concentrations of TMI. We have added this equation in the supplement material.

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

A: Yes, we have changed the word from "intensively" to "rapidly".

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 H_2O_2 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 H_2O_2 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 H_2O_2 due to aerosols, suggesting that there is some considerable uncertainty whether this is the case or not. The PO/O_3 ratio is a good point to make in support of heterogeneous processes being important

A: That is an important question. Based on the current knowledge, unfortunately, we could not give an exact uncertainty of J-values calculated by the TUV model under hazy conditions. In the TUV model 5.0, the aerosol-dependent J-value is estimated using the aerosol optical depth (AOD). We present in the supplement the relationship of AOD and J-values (Fig. S1) and the sensitivity of HO_x and H_2O_2 to AOD (Table S2). It is seen that the J-values for all the photo-sensitive compounds, such as O_3, NO_2, HCHO, and H_2O_2, will decrease by $\sim$50% with an AOD increment of 1, indicating that aerosols could significantly weaken the photolysis of these compounds. The sensitivity analysis shows a decrease of both HO_x and H_2O_2 with increasing AOD. This decrease is more apparent at AOD <2 than that at AOD >2. When we input an AOD value of 2 or even higher into the gas phase model, the calculated H_2O_2 was much higher than the observed H_2O_2 for the heavy haze days. This result suggests that the simple AOD increase (or J-value decrease) could not explain the observed low H_2O_2 on haze

days. Therefore, the heterogeneous reactions of HO_2 and H_2O_2 should be considered. We have added the following statement into Section 3.4.1: "The aerosols could alter the solar radiation intensity, resulting in a variation of HO_x and H_2O_2. A sensitivity analysis for HO_x and H_2O_2 to AOD was made, and the result is shown in Table S2 in the supplement material. It is seen that both HO_x and H_2O_2 was more sensitive to AOD at a lower AOD (<2). This could be explained by the dual role of solar radiation, that is, it impacts on both the source and loss of HO_x and H_2O_2."

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

A: Yes, we have changed the word from "diversity" to "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/HO_2/H_2O_2 are so closely coupled, the absence of VOC measurements must represent a serious 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.

A: We agree that the lack of VOC measurements would result in considerable uncertainty for simulating H_2O_2 and a poor simulation for MHP and PAA. It is unfortunate that the detailed VOC data for the investigated two summers are unavailable. However, based on a literature search we found data regarding the year to year variability in VOC levels as well as the variability between non-haze and haze days. Wang et al. (2010)

reported that the vehicle emission was the major source for NMHCs (non-methane hydrocarbons) in summer Beijing. Lang et al. (2012) analyzed the variation trend of vehicle population and vehicular emission factors in Beijing from 1999 to 2010. In their study, the vehicle population in Beijing increased but the emission factors decreased year by year. As a result, the NMHC emissions showed a slight decreasing trend, decreasing ∼15% in year 2010 compared to year 2007. We made a NMHC comparison between the haze episode (summer 2006 reported by Guo et al., 2012) and the normal days (e.g., 2007 summer reported by Liu et al., 2012), and found no significant difference between the two types of days in concentration and distribution of different types of NHMCs. Combining the above analysis with the vehicle population analysis in the previous manuscript, we suggest that the change for VOCs in Beijing would be expected to a small extent from 2007 to 2011 and between non-haze and haze days. We have added the above statement to the revised manuscript.

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.

A: You are right. We have clarified the text as: "Due to the lack of adequate information, the aqueous reactions of organics and the uptake of H_2O_2 and HO_2 on solid surfaces are not included in the present study."

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

A: Yes, we have done this in the revised manuscript.

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

A: Unfortunately, we did not get direct evidence on the state of aerosols. The aqueous assumption was made in previous studies (e.g., Mao et al., 2010). The ISORROPIA II model (Fountoukis and Nenes, 2007) can give an estimation for the aqueous phase

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state.

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.

A: Yes. We have added the following statement in the revised manuscript: "Note that the uptake coefficients of HO_2 needed on both non-haze and haze days seem much higher compared to the experimentally measured values of <0.01 to 0.40, suggesting that there should be some unknown processes going on."

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.

A: We have clarified the text as: "The average H_2O_2 concentration on haze days is only about 30% of that on non-haze days. We attribute this reduction in H_2O_2 to the attenuation of solar radiation as well as the enhanced heterogeneous reaction occurring on aerosols during the haze episodes." and "The γ_{HO2} needed to meet the measurements is much higher compared to the experimentally measured values, indicating some other processes must be going on."

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.

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A: Yes, we have modified the figure. Please see the revised manuscript.

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

A: Yes, we have modified the figure. Please see the revised manuscript.

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