

Interactive comment on “Observation of atmospheric peroxides during Wangdu Campaign 2014 at a rural site in the North China Plain” by Yin Wang et al.

Anonymous Referee #1

Received and published: 1 June 2016

Overall Comments

This paper presents some interesting ideas and potentially some interesting evidence for direct emissions of peroxides from biomass burning and heterogeneous loss of peroxides. However, it is far from clear how the model was set up, nor how several of the calculated values were derived. This leaves many open questions when it comes to the data analysis. The interpretation appears to focus on some features of the data and ignoring others, without clear justification. Showing more of the data would better justify the selection of the different phases and episodes and would better illustrate how they differed from each other. This would then strengthen the scientific findings.

I have therefore recommended major changes, as I think there are a number of impor-

C1

tant changes that are required to bring the paper up to a scientifically robust standard to be published in ACP.

Specific Comments

In the model description it seems to suggest that the uncertainty in the model is just due to the uncertainty in the observational constraints (line 184-5). What about uncertainties in chemical mechanism - rate coefficients, reaction products, reaction simplifications?

Dry deposition is a major sink for peroxides, especially H₂O₂. What is the uncertainty in the PBL height? Is this included in the total model error?

Assuming that data below the D.L. is equal to the D.L. will lead to an overestimation on average (lines 204-5). I would suggest using a value of 0.5 D.L.

Lines 211-13: If MHP and PAA being about 20% and 5% of the total peroxides in Wangdu is similar to the results from other rural sites in China, then presumably it could also be stated that with 70% of the peroxides in Wangdu being H₂O₂ that Wangdu is also similar to other rural sites in China?

Lines 214-245: It would be helpful to provide more clarity on what is meant by severe pollution episodes (line 214) and haze days (e.g. line 231). PM_{2.5} mass densities are given for the 4 pollution episodes, but what is used to define haze or non-haze days? It would actually be helpful to see time series of the data presented in Figure 2 for the whole campaign for comparison with Fig. 1 and to better justify the selection of the particular phases and episodes. It would also be helpful to mark on the figures, which periods are defined as pollution episodes and which are the phases that are modelled.

Lines 228-230: It states that there was a substantial decline in peroxides during Episode 3, but it looks to me as though their concentrations had already been substantially lower than the previous episodes in the days leading up to episode 3.

Lines 233-4: It states that the peroxides are lower in episode 4 than in the previous

C2

3 episodes, but it looks to me as if their concentrations were already much lower in episode 3.

Regional transport is said to not impact the model results (lines 253-4). It would be good to model episode 4, which was said to be due to regional transport of pollution to demonstrate this – even if this was exhibited by a disagreement between the model and measurements.

Lines 255-262: The data presented in Figure 4 is said to show, for the daytime, an excellent agreement with the modelled data, 1-2 times higher than the measured. Firstly it is not clear if this refers to all the peroxides presented in Fig. 4. Secondly, I would argue that, particularly for MHP and PAA, the difference is often much greater than 2 times. It also needs to be made clear that the model data in Fig. 4 is from the base case, I presume.

In the section 3.2 (lines 267-8) when considering the overestimation of the peroxides concentrations by the model, errors in the source terms are ruled out on the basis that the production terms are constrained by the observations. It needs to be made clear in the Model Description exactly which terms are constrained by the observations. I would also argue that the chemical mechanism for the production of the peroxides is not well understood. Within the MCM many of the rate coefficients of reactions leading to the formation of peroxides are given as generic values (e.g. the rate coefficient for R2), in the absence of species specific measured rates. Furthermore the mechanism used in this modelling study is limited to a subset of reactions containing the reactions of the measured VOCs and subsequent products. Whilst I appreciate this is a sensible modelling approach, the discussion of the results needs to take account of these weaknesses.

The explanation for the night-time discrepancy for Phase 1 (lines 269-280) is attributed to loss on aerosols and the comparison with Beijing refers to haze days and yet Phase 1 is supposedly for the non-haze days. This is very confusing and emphasises my

C3

point above about defining what is meant by a haze day and how this relates to aerosol loading. It states that there is higher aerosol surface area at night concentrations at night. It would be good to present that data. How were the strengths of the missing sinks estimated?

Looking at Fig. 3, and considering the measured-to-model ratio for Phase 2, I am not sure why MHP is singled out, or why 17th June is singled out in line 285. The largest measured values of the peroxides occur on the 16th and the discrepancy for H₂O₂ looks larger than for MHP. What's more the measured-to-model ratio of 7 for MHP on the 17th looks like it might only be a for short time and at other times the agreement is actually rather good.

Lines 288-9: What evidence is there for biomass burning emissions impacting the composition of the air during phase 2? Are there measurements of acetonitrile, for example? (I see this is covered later with the K⁺ concentrations, but it would have been good to have mentioned this much earlier).

Lines 291-3: What is also remarkable to me about phase 3 is that there is a lot of variability from day to day in the amounts of the peroxides modelled. In fact this variability is as big, if not bigger than the differences between Phase 3 and Phase 1. On some days the H₂O₂ and MHP (both modelled and measured) are quite similar for both Phases 1 and 3. I suggest that more could be learnt about the processes affecting the model and measurements by looking at the day to day variability within Phase 3. Did the haze vary much between days? How was the haziness quantified?

Lines 299-305: The text here implies that there were modifications made to the chemical mechanism, with the new reactions given in Table 2. However, it is not clear what they have changed from. New reactions or just new rates?

Lines 321-324: In line 321 it states that the values agree with measurements and then in lines 322-324 say that the additional reactions have marginal impact and are insufficient to match the observations. This is a contradiction as I see it.

C4

When discussing Fig. 3. I would like to see more comment on the shape of the diurnal cycle. The modelled and measured shapes are often very different.

Line 348: The numbers given here are orders of magnitude lower than those for isoprene and trans-2-butene in Fig. 5, so are confusing.

Lines 349-350. This refers to emissions of isoprene and trans-2-butene and yet it is not clear if the model includes emissions. In fact the model description implies that the model is constrained by observed mixing ratio of the VOCs. The model description needs to be much clearer and the text here consistent with the way the model was set up.

Line 368: Whilst I understand that biogenic emissions are not exactly controllable, they can be changed by changes in land use (e.g. different types of vegetation), and policies should consider how such changes could improve or worsen air quality.

It would be helpful to provide a time series of K⁺ concentrations, for the whole of the campaign to illustrate the periods influenced by biomass burning.

It would also be helpful to annotate Figs. 2 and 3, to show the times of the biomass burning events.

Line 403: How were the strengths of the primary sources calculated?

What is the impact of including primary sources of the peroxides on the chemistry? E.g. does it have an impact on HOX? Are the modelled HOX values comparable to observed values and does the addition of primary sources change this comparison?

Lines 410-13: What other removal processes have been ignored that would lead to underestimating the peroxides, other than heterogeneous loss?

Lines 483-498 Given that OH concentrations and photolysis rates will be reduced in the evenings, the lifetimes calculated will be lower than daytime values. Are the modelled values 24 hour averages? It needs to be clear exactly what you are comparing and if

C5

they are for the same times of day. How sensitive are the modelled relative losses (Fig. 6) to uncertainties in the boundary layer height?

Lines 509-513: Just because the model and measured values of HO₂ agree, it doesn't necessarily mean that aerosol uptake of HO₂ is insignificant. What is the impact of including H₂O₂ heterogeneous loss on HO₂?

Minor Comments

Line 270, suggest changing "coincides" to "is consistent".

Lines 305-310: Break this sentence up in to smaller sentences.

Line 326: Change "source" to "sources".

Lines 329-336: The English is hard to follow. Break this sentence up in to smaller sentences.

Line 340: Delete "The".

Line 341: Change "that was disregarded" to "not included".

Line 343: Change "seven" to "the seven".

Line 346: Change "shows strong dependence of alkenes" to "shows a strong dependence on alkenes".

Line 351: The logic implied by the word "Besides" does not make sense to me.

Line 353: Change "Such" to "Such a".

Line 358: Change "between two" to "between the two".

Line 360: Delete "the support on the basis of".

Line 364: Change "for the responsible" to "responsible for the".

Line 387: Change "abundance" to "abundances".

C6

Line 387: Change "increased . . . that" to "were higher than".
Line 388: Change "was" to "is".
Line 395: Change "the concentration of K+ twice more than" to "concentrations of K+ more than twice".
Line 399: Change "the duration" to "durations".
Line 401: Change "observation" to "observations".
Line 404: Change "were" to "are".
Line 421: Change "coincided" to "agreed".
Line 423: Move "relative" to after "PAA".
Line 424: Change "were" to "are".
Line 430: Change "seem to be the" to "are".
Line 424: Change "were" to "are".
Line 438-39: Change "be beneficial" to "help".
Line 444: Change "considerably" to "considerable".
Line 445: Change "made" to "make".
Line 445: Change "of heterogeneous reaction was" to "of the heterogeneous reaction were".
Line 468: Change "heterogeneous" to "the heterogeneous".
Line 489: Change "lifetime" to "lifetimes".
Line 490: Change "whole" to "whole of".
Line 490: Change "was" to "were".

C7

Line 503: Change "referred" to "inferred".
Line 508: Change "are various" to "vary".
Line 516: Delete "is".
Line 517: Change "resulted" to "results".
Line 518: Change "reaction" to "reactions".
Line 532: Change "Wangdu" to "the Wangdu".
Line 536: Change "of" to "of an".
I suggest breaking some of the long paragraphs into shorter ones.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-292, 2016.

C8