

July 3, 2016

Dear Prof. Heard,

Enclosed please find our revised manuscript acp-2016-292 entitled “*Observation of atmospheric peroxides during Wangdu Campaign 2014 at a rural site in the North China Plain*”. We have revised our manuscript according to the two reviewers’ comments and finished the responses to their comments. Detailed, point-by-point responses to the comments and corresponding revisions to the manuscript have been submitted. We believe that the revised manuscript is significantly improved. The changes relative to the preceding manuscript version are specified as followings:

- (1) We have shown time series of meteorological parameters and chemical species during the whole campaign according to the suggestion of the reviewer.
- (2) We have reevaluated the total model error with the uncertainties in chemical mechanism included.
- (3) We have added the definition of haze and non-haze days to justify the selection of haze episode.
- (4) We have provided a time series for K^+ in $PM_{2.5}$ in Fig. 2 as the evidence for the identification of biomass burning event.
- (5) We have adjusted some words, tables, figures and references according to the reviewers’ suggestions. We have deleted the redundant words and sentences to clarify our manuscript.
- (6) Technical points that the reviewers pointed out and we found have been corrected in the revised manuscript.

Attached please find the response to the two reviewers and the revised manuscript with change marks.

Thanks for your time.

Sincerely yours,

Zhongming Chen and co-authors

To Reviewer #1

Thank you very much for your time and constructive comments. Here are our responses to your comments.

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

Reply: Thanks for your constructive and insightful comments, which indeed help us improve our manuscript. In the revised manuscript, we have provided more evidence for discussion as well as clearer descriptions on the method of modeling according to your comments. In the following we respond to your specific comments.

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?

Reply: The uncertainties in chemical mechanism was calculated to be less than 20% according to the method described in Lu et al. (2012).

Dry deposition is a major sink for peroxides, especially H_2O_2 . What is the uncertainty in the PBL height? Is this included in the total model error?

Reply: Dry deposition is not a major sink for peroxides. The uncertainty in the PBL height was estimated to be 25% according to Xu et al. (2013). It is 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..

Reply: Yes, we have replaced the data below the D.L. with half of the D.L. and modified the Table 1, Fig. 1-3. Please see the revised manuscript.

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?

Reply: Yes.

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?

Reply: Yes. In the present work, on the basis of the latest national Ambient Air Quality Standards of China (GB3095-2012), the haze pollution episode is defined as the event that a set of continuous days with daily-averaged PM_{2.5} concentration exceeds 75 µg m⁻³, which has been used to distinguish non-haze and haze episode in the literature (Che et al., 2014; Zhang et al., 2016; Zheng et al., 2015; Zheng et al 2016).

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.

Reply: Yes. We have modified Fig. 2. Please see the revised manuscript.

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.

Reply: Yes. The mean MHP and PAA levels in the days leading up to Episode 3 (27–28 June) and in Episode 3 were comparable, while the mean H₂O₂ level during Episode 3 (0.28 ppbv) declined compared with that on 27–28 June (0.37 ppbv). We have changed the statement from “a substantial decline of H₂O₂, MHP and PAA level” to “a substantial decline of H₂O₂ level”.

Lines 233-4: It states that the peroxides are lower in episode 4 than in the previous 3 episodes, but it looks to me as if their concentrations were already much lower in episode 3.

Reply: Yes. The mean H₂O₂ concentration in Episode 3 (0.28 ppbv) was lower than

that in Episode 4 (0.32 ppbv), but the mean MHP concentration in Episode 3 (0.12 ppbv) was higher than that in Episode 4 (0.09 ppbv). We have changed the statement from “compared with the other three episodes” to “compared with Episode 1 and Episode 2”.

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.

Reply: Yes, we agree. However, it is unfortunate that the detailed VOC data for episode 4 are unavailable. So we do not simulate the concentrations of atmospheric peroxides during episode 4.

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.

Reply: Yes. We have clarified the text as: “the model base case prediction of H₂O₂ level had good performance in the daytime”. We have also clarified the title of Fig. 4 with “the model base case” added.

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.

Reply: Yes. Measurements of NO/NO₂, CO, O₃, HONO, NMHCs, temperature, pressure and H₂O were used as inputs to constrain the model calculations. The measured and modelled HO₂ concentrations at Wangdu site are close to each other. The secondary production terms of atmospheric peroxides including peroxy radical self/cross reactions and the ozonolysis of unsaturated VOCs are constrained by the observations. We have deleted ‘by assuming that the chemical mechanisms of

atmospheric peroxides are well-understood’.

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 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?

Reply: Yes, we have presented the mean surface area concentration at daytime and nighttime. Please see the revised manuscript. The strengths of the missing sinks were quantified by the difference between modelled and measured peroxide concentrations.

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.

Reply: Yes. The measured-to-model ratio of 7 for MHP on 17 June was for about 2 hours. We have deleted “the measurement-to-model ratio based on the model case was up to a factor of 7 for MHP on 17 June, which was much higher than the measurement and model errors”.

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).

Reply: Yes, we have provided a time series for K⁺ in PM_{2.5} in Fig. 2 and mentioned this in Sect. 3.1. Please see the revised manuscript.

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?

Reply: Yes. The haziness was quantified according to the mean PM_{2.5} concentrations over 75 µg m⁻³. The haze on 1 July and 3 July was more serious with the

daily-averaged PM_{2.5} concentrations 1.6 times higher than those on 29 June, 30 June and 2 July. We have added the following statement in the revised manuscript: “The haze arose on 29 June with the elevated PM_{2.5} concentration. The diffusion condition was poor as the CO concentration was enhanced. The precursors of atmospheric peroxides also accumulated on 29 June and 30 June. The modelled peroxide concentrations over 10 times higher than the measured peroxide concentrations. On 1 July and 3 July, the daily-averaged PM_{2.5} concentration was 1.6 times higher than those on 29 June and 30 June. However, the photolysis frequencies and the PBL height on 1 July and 3 July were about half of those on 29 June and 30 June, which weakened the secondary formation of atmospheric peroxides and strengthened the loss of atmospheric peroxides via dry deposition. Although the haze on 1 July and 3 July was more serious than that on 29 June and 30 June, the ratios of modelled to measured peroxide concentrations on 1 July and 3 July were much lower than those on 29 June and 30 June.”.

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?

Reply: For CH₃O₂ related chemistry, the new reaction between CH₃O₂ radicals and HO₂ radicals was incorporated in our box model. For CH₃C(O)O₂ related chemistry, only new rate constants were employed in our box model.

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.

Reply: Yes. We have deleted “Moreover.... errors”.

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.

Reply: Yes. With the inclusion of heterogeneous uptake of atmospheric peroxides, the modelled and measured shapes in the Phase II are different due to the lack of possible primary emission from biomass burning in our box model, while the modelled and measured shapes in the Phase I and the Phase III are similar and can be explained by the model-measurement uncertainty.

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.

Reply: Yes. We have deleted “In.... seen”.

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.

Reply: Yes. The model does not include emissions. We have changed the statement from “isoprene from the local biogenic emission and trans-2-butene from the anthropogenic emission diversity” to “isoprene and trans-2-butene”.

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.

Reply: Yes, we agree. We have clarified the text as: “It is recommended to take measures for vehicle emission control and land use management (e.g. modifying the amount and types of vegetation) in order to mitigate the pollution of atmospheric peroxides in the NCP and hence alleviate their potential harmful effects on air quality, human health and ecosystem”.

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.

Reply: Yes. We have provided a time series for K^+ in $PM_{2.5}$ in Fig. 2. In addition, we have redefined the biomass burning Event II as 16:00–19:00 on 16 June, for it exhibited more excellent correlation with K^+ . We have also modified Table 3. Please see the revised manuscript.

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

Reply: Yes. We have modified Fig. 2-3. Please see the revised manuscript.

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

Reply: The strengths of the primary sources were quantified by the difference between modelled and measured peroxide concentrations.

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

Reply: The impact of primary sources of the peroxides on HO_x radicals was marginal as the primary production of HO_x radicals was dominated by the photolysis of HONO, O_3 , HCHO and dicarbonyls. The change of modelled HO_x values was almost

negligible with the addition of primary sources in our box model. The observed OH concentration was underestimated, while the observed HO₂ concentration was reproduced by the model. More data analysis on the HO_x chemistry can be obtained from Tan et al. (2016).

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

Reply: We think that there is no removal pathway other than heterogeneous loss that would lead to the overestimation of atmospheric peroxides.

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

Reply: Yes. The modelled values were 24 hour averages. The comparison was done for the same times of day. The sensitivity of modelled relative loss of dry deposition to the uncertainties in the planetary boundary layer height was low, for instance, the contribution of dry deposition to the loss of H₂O₂ in Phase I decreased from 17% to 10% with the PBL height doubled. Heterogeneous uptake by aerosols was still the predominant sink for atmospheric peroxides.

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?

Reply: Yes. We have clarified the text as: "the impact of aerosol uptake of HO₂ radicals on the concentration of atmospheric peroxides is insignificant". The impact of H₂O₂ heterogeneous loss on HO₂ radical concentrations was marginal.

Minor Comments

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

Reply: Yes.

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

Reply: Yes, we have broken this sentence into smaller ones.

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

Reply: Yes.

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

Reply: Yes, we have broken this sentence into smaller ones.

Line 340: Delete “The”.

Reply: Yes.

Line 341: Change “that was disregarded” to “not included”.

Reply: Yes.

Line 343: Change “seven” to “the seven”.

Reply: Yes.

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

Reply: Yes.

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

Reply: Yes, we have replaced “Besides” with “Moreover”.

Line 353: Change “Such” to “Such a”.

Reply: Yes.

Line 358: Change “between two” to “between the two”.

Reply: Yes.

Line 360: Delete “the support on the basis of”.

Reply: Yes.

Line 364: Change “for the responsible” to “responsible for the”.

Reply: Yes.

Line 387: Change “abundance” to “abundances”.

Reply: Yes.

Line 387: Change “increased that” to “were higher than”.

Reply: Yes.

Line 388: Change “was” to “is”.

Reply: Yes.

Line 395: Change “the concentration of K^+ twice more than” to “concentrations of K^+ more than twice”.

Reply: Yes.

Line 399: Change “the duration” to “durations”.

Reply: Yes.

Line 401: Change “observation” to “observations”.

Reply: Yes.

Line 404: Change “were” to “are”.

Reply: Yes.

Line 421: Change “coincided” to “agreed”.

Reply: Yes.

Line 423: Move “relative” to after “PAA”.

Reply: Yes.

Line 424: Change “were” to “are”.

Reply: Yes.

Line 430: Change “seem to be the” to “are”.

Reply: Yes.

Line 424: Change “were” to “are”.

Reply: Yes.

Line 438-39: Change “be beneficial” to “help”.

Reply: Yes.

Line 444: Change “considerably” to “considerable”.

Reply: Yes.

Line 445: Change “made” to “make”.

Reply: Yes.

Line 445: Change “of heterogeneous reaction was” to “of the heterogeneous reaction were”.

Reply: Yes.

Line 468: Change “heterogeneous“ to “the heterogeneous”.

Reply: Yes.

Line 489: Change “lifetime“ to “lifetimes”.

Reply: Yes.

Line 490: Change “whole“ to “whole of”.

Reply: Yes.

Line 490: Change “was“ to “were”.

Reply: Yes.

Line 503: Change “referred“ to “inferred”.

Reply: Yes.

Line 508: Change “are various“ to “vary”.

Reply: Yes.

Line 516: Delete “is”.

Reply: Yes.

Line 517: Change “resulted“ to “results”.

Reply: Yes.

Line 518: Change “reaction” to “reactions”.

Reply: Yes.

Line 532: Change “Wangdu” to “the Wangdu”.

Reply: Yes.

Line 536: Change “of” to “of an”.

Reply: Yes.

I suggest breaking some of the long paragraphs into shorter ones.

Reply: Yes, we have broken the long paragraphs into shorter ones. Please see the revised manuscript.

References

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To Reviewer #2

Thank you very much for your careful review.

Observation of atmospheric peroxides during Wangdu Campaign 2014 at a rural site in the North China Plain

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Abstract

Measurements of atmospheric peroxides were made during Wangdu Campaign 2014 at Wangdu, a rural site in the North China Plain (NCP) in summer 2014. The predominant peroxides were detected to be hydrogen peroxide (H_2O_2), methyl hydroperoxide (MHP) and peroxyacetic acid (PAA). The observed H_2O_2 reached up to 11.3 ppbv, which was the highest value compared with previous observations in China at summer time. A box model simulation based on the Master Chemical Mechanism and constrained by the simultaneous observations of physical parameters and chemical species was performed to explore the chemical budget of atmospheric peroxides. Photochemical oxidation of alkenes was found to be the major secondary formation pathway of atmospheric peroxides, while contributions from alkanes and aromatics were of minor importance. The comparison of modelled and measured peroxide concentrations revealed an underestimation during biomass burning events and an overestimation on haze days, which were ascribed to the direct production of peroxides from biomass burning and the heterogeneous uptake of peroxides by aerosols, respectively. The strengths of the primary emissions from biomass burning were on the same order of the known secondary production rates of atmospheric peroxides during the biomass burning events. The heterogeneous process on aerosol particles was suggested to be the predominant sink for atmospheric peroxides. The atmospheric lifetime of peroxides on haze days in summer in the NCP was about 2–3 hours, which is in good agreement with the laboratory studies. Further comprehensive

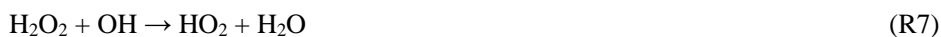
investigations are necessary to better understand the impact of biomass burning and heterogeneous uptake on the concentration of peroxides in the atmosphere.

1 Introduction

Atmospheric peroxides, including hydrogen peroxide (H_2O_2) and organic peroxides (ROOH), are vital oxidants present in the gaseous, aqueous and particulate phase in the atmospheric chemical processes. They serve as temporary reservoirs for HO_x radicals, contributing to the atmospheric oxidation capacity (Reeves and Penkett, 2003). Peroxides also participate in the conversion of S(IV) to S(VI) in the aqueous phase, leading to the acid precipitation and the formation of secondary sulfate (SO_4^{2-}) aerosols in the troposphere (Calvert et al., 1985; Stein and Saylor, 2012). Furthermore, atmospheric peroxides are considered as the key components of secondary organic aerosol (SOA), which play a significant role in the formation and duration of haze pollution (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012; Li et al., 2016). In addition, it has been suggested that atmospheric peroxides are toxic to ecosystem and may be the critical pollutants of forest decline (Hellpointner and G ¨ub, 1989; Chen et al., 2010). More importantly, peroxides in the particle phase have been found to act as reactive oxygen species (ROS) and result in adverse influence on human health (Ayres et al., 2008).

The concentrations of atmospheric peroxides are determined by their production and destruction. The known formation pathways of peroxides in the atmosphere are primary emissions, for instance, biomass burning (Lee et al., 1997, 1998; Yokelson et al., 2009), and secondary sources such as peroxy radical self/cross reactions and the ozonolysis of unsaturated volatile organic compounds (VOCs), as shown in Reaction (R1, R2) and (R3, R4), respectively (Hewitt and Kok, 1991; Neeb et al., 1997; Sauer et al., 2001; Chao et al., 2015; Winiberg et al., 2016). Additionally, atmospheric aqueous reactions in the bulk solution or on the surface of wet particles coupled with subsequent release to the gas phase could also generate peroxides in the troposphere (Wang et al., 2012; Liang et al., 2013a; Zhao et al., 2013a). The typical removal pathways of peroxides in the atmosphere are photolysis (R5, R6), reaction with OH

radicals (R7, R8) and physical deposition (Atkinson et al., 2006; Sander et al., 2011; Nguyen et al., 2015). Heterogeneous uptake by atmospheric aerosols is recognized as another significant sink for peroxides in the troposphere, especially in dusty and polluted urban areas (Zhao et al., 2013b; Wu et al., 2015).



In the past years, a number of field observations, laboratory studies and modelling research have been carried out to investigate the abundance and behavior of peroxides in the atmosphere (Chen et al., 2008; Mao et al., 2010; Huang et al., 2013; Liang et al., 2013a; Sarwar et al., 2013; Epstein et al., 2014; Fischer et al., 2015; Khan et al., 2015). Hydrogen peroxide (H_2O_2), hydroxymethyl hydroperoxide (HMHP, HOCH_2OOH), methyl hydroperoxide (MHP, CH_3OOH) and peroxyacetic acid (PAA, $\text{CH}_3\text{C}(\text{O})\text{OOH}$) are generally determined to be the principal peroxide compounds in the troposphere with their concentrations ranging from pptv (parts per trillion by volume) to ppbv (parts per billion by volume) (Lee et al., 2000; He et al., 2010; Zhang et al., 2010, 2012). However, to date, there have been limited studies concerned with atmospheric peroxides in the regions primarily affected by anthropogenic sources such as the North China Plain (NCP), which is a typical region with frequent biomass burning and suffering from serious haze pollution in China (Tao et al., 2012; Huang et al., 2014). Few numerical simulations focused on atmospheric peroxides in the NCP are conducted to examine whether the models can reproduce the observations of peroxides (Liang et al., 2013a). The impact of biomass burning and high aerosol loading on the atmospheric chemistry of peroxides over such a polluted region is poorly understood. Therefore, this work was carried out in order to make an endeavor

to fill in these research gaps.—

In this study, we present a novel dataset of atmospheric speciated peroxides and explore their atmospheric chemistry at a rural site, Wangdu, which represents regional air pollution conditions of the NCP during Wangdu Campaign 2014. Given the diversity of emission sources and chemical transformation of atmospheric peroxides over this region, it is challenging to analyze the phenomena and understand the primary emission and secondary formation of peroxides in the atmosphere during this field observation. However, with the continuous measurements of atmospheric peroxides, physical parameters and other chemical species performed simultaneously, a quantitative assessment of the budget of atmospheric peroxides can be carried out employing the zero-dimensional model based on Master Chemical Mechanism (MCM) and constrained by observed meteorological parameters and trace gases, which provides a good opportunity to comprehensively facilitate our knowledge of the chemistry of atmospheric peroxides in the NCP. As far as we know, this is the first study to test whether current atmospheric peroxides related chemistry could explain the field observation in the rural area of the NCP. Through the comparison between measurement and simulation, our aim is to investigate the role of biomass burning and heterogeneous uptake on aerosols in the concentration of atmospheric peroxides, which helps to develop more robust mechanism in the model.

2 Experiments

2.1 Measurement site

Measurements of atmospheric peroxides were performed at Wangdu site (38.66 °N, 115.20 °E) in Baoding city, Hebei Province, a rural supersite for the Wangdu Campaign 2014 situated in the northwest of the NCP, about 200 km southwest of the mega-city Beijing. The surrounding regions of Wangdu site are mainly agricultural fields. There are almost no industries near this site. During the summer season, the air pollution is caused by the primary emission from biomass burning and secondary formation including photochemical and heterogeneous processes. The instruments were placed in a container with the sampling inlet approximately 5 m above the

ground. The continuous observation of atmospheric peroxides was conducted from 4 June to 7 July 2014.

2.2 Measurement methods

2.2.1 Measurement method for atmospheric peroxides

Atmospheric peroxide concentrations were investigated by an automated on-site high performance liquid chromatography (HPLC) with post-column enzyme derivatization and detected by fluorescence spectroscopy. Air samples were pumped through a glass scrubbing coil maintained at a controlled temperature of about 4°C to collect the peroxides in the atmosphere. The flow rate of air samples was set to be 2.7 standard L min⁻¹. The stripping solution, 5×10⁻³ M H₃PO₄ in water was delivered into the scrubbing coil collector. The flow rate of stripping solution was set to be 0.2 mL min⁻¹. Once the air samples mixed with the stripping solution in the collector, the mixture was carried by the mobile phase containing 5×10⁻³ M H₃PO₄ at 0.5 mL min⁻¹ and injected into HPLC. The peroxide components were separated after the mixture passed through HPLC column. With the catalysis of Hemin at ~40 °C, the derivatization reaction between peroxide components and para-hydroxyphenylacetic acid (PHPAA) produced the fluorescent matter that can be quantified by fluorescence detector. In this work, atmospheric peroxides were measured every 20 min. The collection efficiencies for hydrogen peroxide and organic peroxides were determined to be 100% and 85%, respectively. The detection limit of peroxides in the gas phase was about 10 pptv.

The interference of SO₂ on the sampling was estimated using the theoretical thermodynamic and kinetic analysis presented in Hua et al. (2008). Considering the rate constant for reaction between peroxides and S(IV) reported by Ervens et al. (2003) and the mean level of SO₂ was 7.0±7.0 ppbv during the campaign, the negative artifact caused by SO₂ interference for peroxides was calculated to be less than 15%. The influence of ambient relative humidity (RH) on the measurement of atmospheric peroxides was calculated following the method introduced by Liang et al. (2013b). The change of the concentration of atmospheric peroxides after this calibration is less

than 10%. Here, we did not correct the observational data for any artifacts due to the uncertainties from the theoretical estimation of peroxides loss that possibly result in new errors. The uncertainty of our observational data is estimated to be ~15%. Further details about our measurement method for atmospheric peroxides can be obtained from Hua et al. (2008).

2.2.2 Measurement methods for other pollutants and parameters

During Wangdu Campaign 2014, SO₂, CO, NO/NO₂ and O₃ were measured concurrently at this supersite using a suite of commercial instruments (Thermo 43i, 42i, 48i and 49i). HONO was measured every 2 min with a LOng Path Absorption Photometer (LOPAP) (Liu et al., 2016). C₂–C₁₀ non-methane hydrocarbons (NMHCs) were analyzed with a time resolution of 60 min by a custom-built online VOC analyzer using automated gas chromatography (GC) coupled with flame ionization detector (FID) or mass spectrometry (MS) technique (Wang et al., 2014). OH and HO₂ radicals were measured by laser-induced fluorescence (LIF) spectroscopy. [\(Tan et al., 2016\)](#). Size distributions of aerosols (PM₁₀) were determined every 10 min with a Twin Differential Mobility Particle Sizer (TDMPS) and an Aerodynamic Particle Sizer (APS) to calculate dry particle surface area concentrations (S_a). Hygroscopic growth factor, f (RH), which is defined as the ratio of scattering coefficient for ambient aerosol to scattering coefficient for dry aerosol, was derived from the integrating nephelometer (Liu, 2015). Measurements of the mass concentration of PM_{2.5} were obtained by TEOM 1400A analyzer. [Water-soluble ions \(i.e., NH₄⁺, K⁺, Cl⁻, SO₄²⁻ and NO₃⁻\) in PM_{2.5} was measured every 30 min with a Gas and Aerosol Collector \(GAC\) \(Ye, 2015\)](#). Photolysis frequencies were derived from a spectro-radiometer (Bohn et al., 2008). Meteorological parameters including ambient temperature, relative humidity (RH), pressure, wind speed, wind direction and rainfall were monitored continuously by a weather station. The uncertainties (1σ) in these measurements are estimated as 5% for NO, O₃, and CO, 10% for H₂O, NO₂, HONO, NMHCs, and solar radiation, and 20% for S_a .

2.3 Model description

A zero-dimensional box model using a near-explicit mechanism, MCM Version 3.3.1 (<http://mcm.leeds.ac.uk/MCM/>) (Jenkin et al., 1997, 2003; Saunders et al., 2003; Jenkin et al., 2015) was employed to examine the influence of biomass burning and heterogeneous uptake on the budget of atmospheric peroxides. MCMv3.3.1 describes the degradation of 143 VOCs, leading to about 5800 species and 17000 reactions. In the current study, we extracted a subset of MCMv3.3.1 containing the reactions of atmospheric oxidants with measured VOCs and subsequent chemical products. Measurements of NO/NO₂, CO, O₃, HONO, NMHCs, temperature, pressure and H₂O were used as inputs to constrain the model calculations. The model ran with a 5-min time step and a spin-up time of 2 days to reach a steady state.—

Photolysis frequencies were calculated by the Tropospheric Ultraviolet and Visible (TUV, version 5.2) model (Madronich, 2002), and further rescaled with the measured $j(\text{NO}_2)$. Dry deposition velocities of trace gases in our box model were parameterized as V_d/h (Seinfeld and Pandis, 2006), where V_d is the dry deposition rate of species and h is the height of planetary boundary layer (PBL). Dry deposition rates of HNO₃, PANs, organic nitrates, H₂O₂, organic peroxides and aldehydes incorporated in the model were set as $2.0 \times 10^{-5} \text{ s}^{-1}$, $5.0 \times 10^{-6} \text{ s}^{-1}$, $1.0 \times 10^{-5} \text{ s}^{-1}$, $1.0 \times 10^{-5} \text{ s}^{-1}$, $5.0 \times 10^{-6} \text{ s}^{-1}$ and $1.0 \times 10^{-5} \text{ s}^{-1}$, respectively at the PBL height of 1 km (Zhang et al., 2003; Emmerson et al., 2007; Lu et al., 2012; Guo et al., 2014; Li et al., 2014c; Liu et al., 2015; Nguyen et al., 2015). The PBL height over Wangdu during this campaign was derived from the hybrid single-particle lagrangian integrated trajectory (HYSPLIT) model (Draxler and Rolph, 2012), which varied between about 300 m at midnight and over 3000 m at noon.—

The uncertainty of our model calculation derives from the uncertainty of observational data, [PBL height and reaction rate coefficients in chemical mechanism](#). The total uncertainty in the model was estimated from the errors of all input parameters using error propagation, which is similar to the method that can be found in Hofzumahaus et al. (2009). On average, the modelled concentration of atmospheric peroxides had an uncertainty of approx. ~~40%~~60%.

In the present study, to explore the impact of the heterogeneous process on the

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concentration of atmospheric peroxides, our box model is extended with the aerosol uptake of peroxides. The pseudo-first-order rate constant for the heterogeneous uptake of peroxides on ambient aerosols is parameterized as follows:

$$k = \frac{1}{4} \gamma \cdot v \cdot S_{aw} \quad (1)$$

(Jacob, 2000), where γ is the uptake coefficient, v is the mean molecular velocity, S_{aw} is the aerosol surface concentration corrected by the measured hygroscopic factor, $f(\text{RH})$ that could be expressed as $S_{aw} = S_a \times f(\text{RH})$.

3 Results and Discussion

3.1 General observations

The concentrations of peroxides in the atmosphere were measured continuously from 4 June to 7 July 2014. The predominant peroxides over Wangdu included H_2O_2 , MHP and PAA. Time series for atmospheric peroxides during Wangdu Campaign 2014 are illustrated in Fig. 1. The statistical data about the observed concentration of atmospheric peroxides are summarized and given in Table 1. It should be noted that values below the detection limit (D.L.) of our instrument were replaced by [half of the corresponding](#) D.L. in Fig. 1, Fig. 2 and statistical calculations. In this study, H_2O_2 accounted for ~70% of total detected peroxides ($\text{H}_2\text{O}_2 + \text{MHP} + \text{PAA}$). However, in our previous work, H_2O_2 contributed not more than 30% of total peroxides in the atmosphere over urban Beijing at the summer time of 2010 and 2011 (Liang et al., 2013b). This might be caused by the difference on the production and destruction of atmospheric peroxides between two sites. MHP and PAA were determined to be about 20% and 5% of total peroxides over Wangdu, respectively, which is similar to the results of other rural sites in China from our previous investigations (Zhang et al., 2010, 2012).

~~During this campaign, there were four severe~~[In the present work, on the basis of the latest national Ambient Air Quality Standards of China \(GB3095-2012\), the haze pollution episode is defined as the event that a set of continuous days with daily-averaged \$\text{PM}_{2.5}\$ concentration exceeds \$75 \mu\text{g m}^{-3}\$, which has been used to](#)

[distinguish non-haze and haze episode in the literature \(Che et al., 2014; Zhang et al., 2016; Zheng et al., 2015; Zheng et al 2016\)](#). During this campaign, there were four [haze](#) pollution episodes at Wangdu site as follows: Episode 1 (4 June–6 June), Episode 2 (12 June–17 June), Episode 3 (29 June–3 July) and Episode 4 (5 July–7 July) with elevated average PM_{2.5} concentrations (75 $\mu\text{g m}^{-3}$, 92 $\mu\text{g m}^{-3}$, 79 $\mu\text{g m}^{-3}$ and 99 $\mu\text{g m}^{-3}$, respectively). In Episode 1, H₂O₂, MHP and PAA were observed up to 11.3 ppbv, 0.9 ppbv and 1.5 ppbv, respectively. The maximum H₂O₂ concentration on 5 June was the highest value so far among the previously reported observations in urban, suburban and rural areas in China at summer time. The possible reason for this peak concentration at Wangdu site could be the primary emission from biomass burning combined with the secondary formation by the intense photochemical process. Nevertheless, owing to the lack of supporting data for other pollutants and parameters, it is difficult to identify the relative contributions of biomass burning versus photochemical formation to the burst of atmospheric peroxides on 5 June. In Episode 2, there was widespread and intensive biomass burning in the NCP as this observation period covered the local wheat harvest season. [The evidence for biomass burning from the measurement of K⁺ in PM_{2.5} was illustrated in Fig. 2](#). The sudden raise of atmospheric peroxides was observed and further discussed in Sect. 3.3. In Episode 3, there was a substantial decline of H₂O₂, ~~MHP and PAA~~ level during this typical haze event compared with the foregoing two episodes, which can be ascribed to the heterogeneous uptake of peroxides on atmospheric aerosols on haze days over Wangdu (See Sect. 3.4). In Episode 4, Wangdu was significantly impacted by the regional transport (Ye, 2015). The concentrations of atmospheric peroxides remained relatively low compared with ~~the other three episodes~~ [Episode 1 and Episode 2](#). In addition to the above-mentioned episodes, it was relatively clear between 8 June and 11 June and 27 June and 28 June, with mean PM_{2.5} concentrations under 40 $\mu\text{g m}^{-3}$. The intermittent thunderstorm activities occurred from 19 June to 25 June that caused the electric power failure and several data gaps.

3.2 Peroxide simulation

In this study, we employed a box model based on the MCMv3.3.1 to simulate H₂O₂, MHP and PAA concentrations. Here, to explore the atmospheric chemistry of peroxides on non-haze, biomass burning and haze days, the observational data from 8 June to 11 June (Phase I), from 15 June to 17 June (Phase II) and from 29 June to 3 July (Phase III) in 2014 were selected as phase of interest and analyzed in detail using box model in the following sections. The temporal variations of meteorological parameters, chemical species and atmospheric peroxides for ~~these three phases~~[the whole campaign](#) are displayed in Fig. 2. The observed and calculated levels of atmospheric peroxides for the three phases are illustrated in Fig. 3. During these case study phases, 75% of the wind speed data were $\leq 2.2 \text{ m s}^{-1}$ and the mean value was 1.6 m s^{-1} . It has been shown that the atmospheric lifetimes of peroxides are on the order of several hours as reported previously (He et al., 2010; Wu et al., 2015), implying that the effect of regional transport or dilution on the concentrations of atmospheric peroxides was of little significance over Wangdu. Hence, the regional-scale transport can be excluded in our box model and the budgets of peroxides are, to a large extent, dependent on local chemical processes during the observation.–

In the Phase I, as shown in Fig. 4, the model [base case prediction of H₂O₂ level](#) had good performance in the daytime (06:00–18:00 local time), which was 1–2 times higher than the measurement results. This seems to be explained by the model-measurement uncertainty. Similarly, a previous observation carried out at a suburban site also showed reasonable model-measurement agreement in H₂O₂ level on sunny days (Guo et al., 2014). The excellent description yielded by the model base case indicated that the production and destruction of ~~atmospheric peroxides~~[H₂O₂ in the atmosphere](#) on non-haze days were calculated correctly based on the current understanding of atmospheric peroxide related chemistry. However, the simulation in the nighttime (18:00–06:00 local time) during the Phase I demonstrated an obvious overestimation compared to the observation by a factor of 4–6 and up to an order of magnitude. This large discrepancy between calculated and observed results is speculated to be resulted from the underestimation of sink terms as the key precursors

governing the formation of atmospheric peroxides are constrained by the observation and the overestimation of source terms can be ruled out ~~by assuming that the chemical mechanisms of atmospheric peroxides are well understood. It coincides.~~ It is consistent with the comparison of the simulated and observed H₂O₂ concentration over urban Beijing, in which the explanation for the overprediction of H₂O₂ level on haze days was thought to be the heterogeneous processes on liquid or solid particles that were missing from the current atmospheric chemistry model (Liang et al., 2013b). Considering the high aerosol loading in the NCP and the higher aerosol surface area concentration at nighttime (1158 μm² cm⁻³) than that at daytime (773 μm² cm⁻³) in the Phase I, we believe that the missing sink for atmospheric peroxides in the model base case is probably heterogeneous uptake of peroxides occurring on aerosols. The ~~strengths~~ strengths of the missing ~~sinks~~ sinks for H₂O₂, MHP and PAA quantified by the difference between modelled and measured peroxide concentrations were ~~estimated to be about~~ 0.24 ppbv h⁻¹, 0.09, ppbv h⁻¹ and 0.03 ppbv h⁻¹ on average, respectively, which ~~was~~ were on the same order of magnitude as the known loss rates of atmospheric peroxides during the Phase I.

In the Phase II, the comparison of the modelled and measured peroxide concentrations in Fig. 3 displays that the observed magnitude of atmospheric peroxides was unexpectedly large, indicating a missing source for peroxides. Such a strong imbalance was found only in the Phase II during the whole campaign, ~~and the measurement to model ratio based on the model case was up to a factor of 7 for MHP on 17 June, which was much higher than the measurement and model errors.~~ In the past, the higher-than-expected concentrations of atmospheric peroxides have also been reported by Lee et al. (1997), in which H₂O₂, MHP, PAA and other organic peroxides levels elevated near biomass burning plumes. Given the frequent fire emissions in the NCP during the Phase II that are quite similar to the conditions in Lee et al. (1997), it appears that the significant mismatch can be attributed to the direct production from biomass burning (See Sect. 3.3).

In the Phase III, the calculated values in the model base case showed a general tendency to strongly overestimate the observed values (Fig. ~~3~~ 3). The haze arose on

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29 June with the elevated PM_{2.5} concentration. The diffusion condition was poor as the CO concentration was enhanced. The precursors of atmospheric peroxides also accumulated on 29 June and 30 June. The modelled peroxide concentrations over 10 times higher than the measured peroxide concentrations. On 1 July and 3 July, the daily-averaged PM_{2.5} concentration was 1.6 times higher than those on 29 June and 30 June. However, the photolysis frequencies and the PBL height on 1 July and 3 July were about half of those on 29 June and 30 June, which weakened the secondary formation of atmospheric peroxides and strengthened the loss of atmospheric peroxides via dry deposition. Although the haze on 1 July and 3 July was more serious than that on 29 June and 30 June, the ratios of modelled to measured peroxide concentrations on 1 July and 3 July were much lower than those on 29 June and 30 June. As there was a typical haze event during the Phase III, the model-measurement imbalance was probably due to the missing sink for atmospheric peroxides, which was the same deficiency in the model as that in the Phase I. It can be seen in Fig. 3 that with the inclusion of heterogeneous reactions on aerosol particles, the simulated concentrations of atmospheric peroxides were apparently improved, which is further quantified in Sect. 3.4.

Before exploring the impact of biomass burning and heterogeneous uptake on the chemistry of atmospheric peroxides, we performed a model test by implementing the newly proposed chemical mechanisms for CH₃C(O)O₂ and CH₃O₂ related chemistry in MCMv3.3.1, as listed in Table 2. The rate constant and the branching ratios of the CH₃C(O)O₂ + HO₂ reaction that was the major pathway for the formation of PAA in this model scenario were modified according to the recent laboratory study conducted by Winiberg et al. (2016). Additionally, we also incorporated the reaction between CH₃O₂ radicals and OH radicals ~~that, which~~ has as yet seldom been involved in atmospheric chemistry model ~~because it was~~. The reaction between CH₃O₂ radicals and OH radicals is recognized as an important sink for CH₃O₂ radicals with non-negligible effect on subsequent formation of MHP under remote conditions ~~by (Bossolasco et al. (., 2014) and; Fittschen et al. (., 2014), in spite of the fact that the reaction product is still unknown).~~ As shown in Fig.3, the model run containing

newly-proposed mechanisms did not have a remarkable influence on the simulated results of H₂O₂ in comparison to the model base case. But a slight difference of up to ~20% between calculated and observed MHP can be noted at night, resulting from the additional removal pathway of CH₃O₂ radicals from the noon to the sunset. The increase of over 70% in rate constant and the reduction of about 10% in the branching ratio of the reaction $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH}$ generated systematically 1.5 times higher PAA concentration in this model scenario than that in the model base case. Nevertheless, although the modelled PAA during the Phase II can be raised close to the level of the observation, the concentrations of atmospheric peroxides were not fully captured by the model with the implementation of newly proposed mechanisms (Fig. 3). ~~Moreover, the resulting MHP and PAA values still agreed with the measurements in the range of their errors. Thus, we can conclude that the~~The additional chemical mechanisms embedded in the model only have a marginal impact that is not sufficient to match the observed peroxides in the atmosphere. The efficient source or sink for the reproduction of the observation will be deeply investigated below.

As outlined in the introduction, the ~~sources~~sources of H₂O₂, MHP and PAA are the direct emission from biomass burning and the photochemical oxidation of VOC precursors via HO₂, CH₃O₂ and CH₃C(O)O₂ formation. However, it is still difficult to determine the contributions of VOC precursors at a species level. Here, to gain further insight into the secondary chemical transformation of atmospheric peroxides at Wangdu site, the sensitivity study ~~with an~~was conducted to track out the major VOC precursors of atmospheric peroxides. An indirect approach ~~adopted~~referring to the relative incremental reactivity (RIR) concept for ozone formation in Cardelino and Chameides (1995) was ~~utilized to track out~~adopted for the ~~major VOC precursors of atmospheric peroxides and assess their roles by~~sensitivity study using the numerical model with the application of the MCMv3.3.1 ~~that can describe~~. MCM describes the explicit degradations of individual VOC species, and hence facilitates to quantify ~~their contributions individually~~the role of VOC in the secondary formation of atmospheric peroxides at a species level. In this work, the definition of RIR is the ratio of

reduction in the production rates of atmospheric peroxides to the reduction of VOC precursor abundances by 25% compared to the model base case, which can be regarded as a proxy for the influence of a specific VOC on the *in-situ* formation of atmospheric peroxides. ~~The~~ Phase I and Phase III were selected for the analysis, while the Phase II was precluded from the analysis as it was affected by the local emission ~~that was disregarded~~ not included in the model base case.—

Fig. 5 displays the average RIRs of H₂O₂, MHP and PAA for alkane, alkene, aromatic and NO_x classes as well as the seven most important individual VOC precursors. The results demonstrate that the formation of H₂O₂ was sensitive to alkenes and insensitive to alkanes, aromatics and NO_x. The production of MHP and PAA shows a strong dependence ~~of~~ on alkenes and NO_x, while it is relatively independent of aromatics and alkanes other than methane. ~~In terms of VOC species with relatively high RIR that is more than 0.001 for H₂O₂ as well as more than 0.01 for MHP and PAA, it is seen that isoprene from the local biogenic emission~~ Isoprene and trans-2-~~butene from the anthropogenic emission~~ butenes turn out to be the key VOC species controlling the formation of atmospheric peroxides. ~~Besides~~ Moreover, cis-2-butene, cis-2-pentene, propene and 1,2,4-trimethylbenzene also seem to be the major individual VOC precursors as evidence by Fig. 5. Methane is noticed to be an important contributor to the formation of MHP. Such a list of VOC species is not consistent with our previous studies over urban Beijing that suggested aromatics (i.e., toluene and dialkylbenzenes) as the dominant VOC precursor of atmospheric peroxides (Zhang et al., 2010; Liang et al., 2013b). It reflects that the relative significance of individual VOC precursors varies from place to place. The distinction between the two sites is attributable to the relatively more abundant isoprene, anthropogenic alkenes and much less reactive aromatics at the rural site in the NCP than those at the urban site, Beijing.—

With ~~the support on the basis of~~ the identification of a small class of key VOC precursors contributing to the formation of peroxides in the atmosphere of NCP, the effective control strategies for mitigating the pollution resulted from atmospheric peroxides can be formulated. In the NCP, it has been revealed that the vehicular

exhaust is the predominant source ~~for the~~ responsible for the VOC species such as propene, trans/cis-2-butenes and trimethylbenzenes in the surrounding areas of the observation site (Yuan et al., 2009; Ran et al., 2011; Li et al., 2014b; Li et al., 2015; Wu et al., 2016), while the vegetation governs the release of isoprene. ~~Taking into account the fact that biogenic emissions of isoprene are not controllable, it~~ It is recommended to take measures for vehicle emission ~~reduction~~ control and land use management (e.g. modifying the amount and types of vegetation) in order to mitigate the pollution of atmospheric peroxides in the NCP and hence alleviate their potential harmful effects on air quality, human health and ecosystem.

3.3 Direct production of peroxides from biomass burning

In the Phase II, the levels of H₂O₂, MHP and PAA were highly elevated in comparison with the other phases, which could not be explained by the photochemical process in the model base case alone. It provides us a hint that an additional formation pathway is required to improve the results of model simulation. In Sect. 3.2, we hypothesized that the direct production of peroxides from biomass burning should serve as an essential source for the unexpected burst of atmospheric peroxides. Here, we tested the hypothesis by means of the box model and linear regression with the observation data from three events mentioned below during the Phase II. It is well known that CO and K⁺ can be used as the reference for the biomass combustion (Koppmann et al., 2005; Reid et al., 2005; Li et al., 2007; Sullivan et al., 2008; Cheng et al., 2013, 2014; Li et al., 2014a; Wang et al., 2015). The averaged CO levels were 0.42±0.16 ppmv, 0.79±0.20 ppmv and 0.61±0.20 ppmv for the Phase I, Phase II and Phase III, respectively. The mean K⁺ concentrations were about 0.64±1.19 µg m⁻³ for the Phase I, 2.51±1.53 µg m⁻³ for the Phase II and 0.26±0.21 µg m⁻³ for the Phase III. The ~~abundance~~ abundances of CO and K⁺ during the Phase II ~~increased apparently compared with~~ were higher than that during the Phase I and Phase III, which ~~wasis~~ consistent with the observed intensive biomass burning activities at Wangdu site (Ye, 2015). Nevertheless, in addition to the biomass burning, CO level in the NCP was also affected by anthropogenic activities with the regional transport of polluted air

masses, for example, the urban plumes. It has been proved that airborne K^+ is acceptable as the tracer for biomass burning during summertime in the NCP (Cheng et al., 2013; Wang et al., 2015). [The concentrations of \$CH_3CN\$, another tracer for biomass burning, measured by Proton-transfer-reaction mass spectrometry \(PTR-MS\) exhibited similar temporal variation to the concentrations of \$K^+\$ during the Wangdu campaign 2014 except on 10 June \(X. Huang, personal communication, 2015\).](#)

Therefore, K^+ might be a better indicator of biomass burning than CO here. In the Phase II, we identified several biomass burning events with ~~the concentration~~[concentrations](#) of K^+ ~~twice~~-more than [twice](#) the mean value of that in the Phase I and Phase III. Considering the availability of the observation data for atmospheric peroxides, we focused our analysis on three events as follows: Event I (17:00–20:00 on 15 June), Event II (~~22~~[16:00–19:00](#) on 16 June ~~1:00 on 17 June~~) and Event III (12:00–15:00 on 17 June) with ~~the duration~~[durations](#) of over 3 hours.

As illustrated in Fig. 3, the model base case cannot reproduce the measurements for atmospheric peroxides in the three events. To match the ~~observation~~[observations](#), the primary sources for H_2O_2 , MHP and PAA were applied to our model. The strengths of the primary sources [for \$H_2O_2\$, MHP and PAA quantified by the difference between modelled and measured peroxide concentrations](#) were ~~calculated to be~~ about 0.25–~~0.98~~[1.80](#) ppbv h^{-1} , 0.~~09~~[24](#)–0.44 ppbv h^{-1} and 0.02–~~0.14~~[16](#) ppbv h^{-1} ~~for H_2O_2 , MHP and PAA~~, respectively. These values ~~were~~[are](#) on the order of the known secondary production rates of atmospheric peroxides during the three events. It should be pointed out that the estimation was associated with large uncertainties since it did not include the heterogeneous uptake of peroxides by aerosols in the model here. In view of the possible additional sink for atmospheric peroxides as discussed in Sect. 3.4 below, the primary sources for H_2O_2 , MHP and PAA might represent the lower limit. The effect of biomass burning on the levels of atmospheric peroxides might be underestimated as well. We underscore that there might exist even larger missing sources for H_2O_2 , MHP and PAA due to the scarcity of some important removal pathways of atmospheric peroxides in the model in this section.

The results of linear regression involving correlation coefficients and their

statistical significance of H₂O₂, MHP and PAA to CO and K⁺ were listed in Table 3 for the three biomass burning events. The relationships between atmospheric peroxides and biomass burning indicators were analyzed separately for each event owing to the variability of fire emissions. A notable trend between atmospheric peroxides and K⁺ was found with correlation coefficients exceeding over the significance threshold, which provided a convincing evidence for the direct production of peroxides from biomass burning as the additional source. Moreover, it was noticed that CO ~~coincided~~agreed well with K⁺ for the Event I and Event II, exhibiting excellent correlation with atmospheric peroxides (Table 3). The enhancement ratios ~~relative~~ of H₂O₂, MHP and PAA relative to CO were calculated to be at the magnitude ~~ranging from~~ of 10⁻³ ~~to~~ 10⁻², which ~~were~~are similar to the enhancement signals of atmospheric peroxides to CO obtained near biomass fires from flights published by Lee et al. (1997).

It is noteworthy that several other chemical processes, for example, secondary formation via the photooxidation of potential unmeasured short-lived VOC species emitted from biomass fires prior to our sampling of the plume at the observational site ~~seem to be the~~are alternatives to the direct production from biomass burning as the missing source of atmospheric peroxides in the model. Thus, it appears necessary and desirable to further distinguish the extent to which atmospheric peroxides are generated via the direct production or secondary formation from biomass burning in future research. Laboratory studies are required to simulate the biomass fires in the NCP using combustion chamber to critically characterize the emission factors of atmospheric peroxides to CO and determine their generation mechanisms. Also, more reliable aircraft and ground-based field measurements for the variation of atmospheric peroxides during the harvest seasons in China need to be carried out and would ~~be~~ beneficialhelp to shed some light on the role of biomass burning in the abundance of peroxides in the atmosphere.

3.4 Heterogeneous uptake of peroxides by aerosol

In Sect. 3.2, heterogeneous uptake on atmospheric particles was considered as a

suitable explanation for the missing sink for H₂O₂, MHP and PAA during the Phase I and Phase III in view of substantial aerosol loading in the NCP that provided ~~considerably~~considerable sites for heterogeneous reactions. Here, we ~~made~~make an attempt to implement a parameterization of heterogeneous uptake by aerosols in our box model to resolve the deviation between the simulated and observed data (See Sect. 2.3). Using the uptake coefficient of 1×10^{-3} for H₂O₂, MHP and PAA, a good agreement between the modelled and measured temporal variation of atmospheric peroxides can be obtained in Phase I and Phase III by taking into account the combined model-measurement error that is conservatively assumed to be ~50% (Fig. 3). The calculated H₂O₂, MHP and PAA with the coupling of ~~the~~ heterogeneous reaction ~~was~~were on average decreased by about 75% compared to the results in the model base case during the Phase III. The uptake coefficient of 1×10^{-3} approached the upper limit of the laboratory measured value for H₂O₂ on mineral dust (9×10^{-4}) reported by Pradhan et al. (2010), but a little higher than the previous measured values on ambient PM_{2.5} of $(1-5) \times 10^{-4}$ during the summertime over urban Beijing (Wu et al., 2015). It is reasonable as Wu et al. (2015) pointed out that the uptake coefficients for H₂O₂ and organic peroxides on ambient PM_{2.5} are in the same range and show no obvious differences between daytime and nighttime or between non-hazy and hazy conditions.

With the adoption of heterogeneous uptake coefficients of 1×10^{-3} , we evaluated the sinks of atmospheric peroxides in the Phase I and Phase III that represented non-haze and haze conditions, respectively. The mean surface area concentration that was corrected for the hygroscopic growth of aerosol was measured to be $968 \mu\text{m}^2 \text{cm}^{-3}$ for Phase I and $1491 \mu\text{m}^2 \text{cm}^{-3}$ for Phase III. Fig. 6 demonstrated that the destruction of atmospheric peroxides during the two phases originated from a diversity of sinks, including photolysis, OH-initiated reaction, dry deposition and heterogeneous uptake. It has been reported that ~~the~~ heterogeneous reaction is the most important sink for H₂O₂ in urban (Liang et al., 2013b) and suburban areas (Guo et al., 2014). In contrast, OH-initiated reaction and dry deposition were regarded as the major removal

pathways of organic peroxides in rural (Zhang et al., 2012) and forests areas (Nguyen et al., 2015). Here, heterogeneous uptake by aerosols turned out to be the predominant sink for atmospheric peroxides in the NCP, accounting for more than 60% of the total loss, while dry deposition became the marginal removal pathway that contributed ~10% to the destruction of H₂O₂, MHP and PAA. The role of OH-initiated reaction in the total loss varied between the speciated peroxides with no more than 30%. Photolysis only represented a minor contribution (<3%). The most prominent feature on haze days was the larger loss of atmospheric peroxides via heterogeneous process, demonstrating the enhanced impact of aerosols on the sink of peroxides during the haze episode compared to that during the non-haze episode.–

On the basis of the analysis above, we investigated the atmospheric lifetime of peroxides in the NCP with the integration of observation and modelling. The lifetime of H₂O₂, MHP and PAA were estimated with the concentration-to-time curves between 18:00 and 24:00 LT as the formation of atmospheric peroxides was weak and negligible during this phase. The average lifetime obtained from the field observation between 18:00 and 24:00 LT in the Phase I was around 4.0 h, 5.6 h and 3.1 h for H₂O₂, MHP and PAA, respectively, which was similar to the values of 3.4 h, 4.3 h and 5.2 h for H₂O₂, MHP and PAA, respectively, given by our modeling simulation. The lifetime of atmospheric peroxides in the Phase III was ~40% smaller than that in the Phase I. Using the box model, the atmospheric ~~lifetime~~lifetimes of H₂O₂, MHP and PAA during the whole ~~of~~ Phase I and Phase III ~~was~~were calculated to be about 2.1 h, 2.3 h and 3.0 h, respectively. This is comparable to the literature results with the inclusion of heterogeneous reaction (Liang et al., 2013b; Wu et al., 2015), but notably shorter than the recent studies conducted by Khan et al. (2015) and Nguyen et al. (2015) without the coupling of the heterogeneous process. The simulated lifetime of atmospheric peroxides can be over 10 h by supposing that the loss of H₂O₂, MHP and PAA is merely due to photolysis, OH-initiated reaction and dry deposition. It emphasizes that heterogeneous uptake on aerosols determines the atmospheric lifetime of peroxides.–

It is worth noting that the heterogeneous uptake of peroxides by aerosols in the atmospheric chemical model is still controversial as it is possibly that the aerosol uptake of HO₂ radicals is the explanation for the missing sink. This raises an interesting question of whether HO₂ uptake or peroxide uptake is responsible for the imbalance between observation and modelling. It has been ~~referred~~inferred by formerly published literature that aerosol uptake of HO₂ radicals is the major reason for the overprediction of the levels of atmospheric peroxides in the model (de Reus et al., 2005; Mao et al., 2013; Guo et al., 2014). Nevertheless, it is apparent that the extent of HO₂ heterogeneous degradation depends on the atmospheric environment, especially the concentration and property of aerosol particles that ~~are various~~vary under different conditions. The measured ~~and modelled~~ HO₂ concentrations at Wangdu site are close to ~~each other, implying that the budget of modelled HO₂ is well captured~~concentrations by the box model merely with the gas-phase regional atmospheric chemical mechanism (RACM) comprised (K. Lu, personal communication, 2015). Hence, the impact of aerosol uptake of HO₂ radicals on the concentration of atmospheric peroxides is insignificant during Wangdu Campaign 2014 and not taken into account in our model, while heterogeneous uptake of atmospheric peroxides by aerosols is exclusively adopted to improve the reproduction of the observation in the two phases above.—

It has been inferred that heterogeneous uptake of peroxides on ambient PM_{2.5} ~~is~~ probably ~~resulted~~results from solid surface reactions and aerosol aqueous reactions (Wu et al., 2015), for instance, “Fenton-like” ~~reaction~~reactions between peroxides and transition metal ions, which is supported by the laboratory studies (Chevallier et al., 2004; Deguillaume et al., 2005) and field observation (Liang et al., 2013b; Guo et al., 2014). Nevertheless, the detailed heterogeneous mechanism containing individual reaction channels was not included in the present work owing to the chemical complexity of the ambient aerosol. Given the potential importance of atmospheric peroxide compounds on the generation of HO_x radicals and aerosol ROS, the aging of mineral dust and SOA and the formation of haze (Huang et al., 2015; Pöschl and

Shiraiwa, 2015; Zhang et al., 2015; Li et al., 2016), more comprehensive investigations including laboratory, field and modelling studies on the heterogeneous uptake processes of H₂O₂, MHP, PAA and other peroxides are indispensable to provide concrete evidence to elucidate the chemical budget of atmospheric peroxides in the future.

4 Conclusions

Atmospheric peroxides including H₂O₂, MHP and PAA were measured at a rural site during [the](#) Wangdu Campaign 2014. The maximum H₂O₂ concentration was observed to be 11.3 ppbv, which was the highest value compared with previous observations in China. The concentrations of atmospheric peroxides were highly elevated during the biomass burning activities, but underwent substantial decline during the haze events. With the application of [an](#) observation-based model combining measured meteorological parameters and trace gases, we analyzed the chemical budget of peroxides under biomass burning, non-haze and haze conditions. Photochemical formation of atmospheric peroxides was attributed to a small class of alkenes, while it was insensitive to alkanes and aromatics. The key VOC precursors controlling the formation of peroxide compounds were identified to be isoprene, trans/cis-2-butenes, cis-2-pentene, propene and trimethylbenzene.—

The base model simulation (MCMv3.3.1) underpredicted the levels of atmospheric peroxides ~~up to a factor of 7~~ during biomass burning events compared with the measurement. The direct production from biomass burning was regarded as the explanation for the unexpected burst of peroxides. To improve the simulated concentrations, the strengths of the primary emissions from biomass burning should be on the same order of the known secondary production rates of atmospheric peroxides. Moreover, the model base case also overpredicted the concentrations of atmospheric peroxides on haze days in comparison with the observation. The heterogeneous uptake by aerosols was suggested to be responsible for the attenuation of peroxides. The model could reproduce the observed values with the introduction of heterogeneous process using the uptake coefficient of 1×10^{-3} for atmospheric

peroxides. According to the closure between observed and calculated concentrations, the heterogeneous uptake on aerosol particles was found to be the predominant sink for atmospheric peroxides, accounting for more than 60% of the total loss, followed by the OH-initiated reaction (<30%) and dry deposition (~10%). The mean atmospheric lifetime of peroxides in summer in the NCP was estimated to be around several hours that was in good agreement with previous laboratory studies for the aerosol uptake of peroxides, indicating that heterogeneous reaction determines the atmospheric lifetime of peroxides.–

In view of the importance of peroxides in tropospheric oxidation capacity and formation potential of secondary aerosols, more reliable investigations focused on the biomass burning emission factors and detailed heterogeneous mechanism of speciated peroxides are urgently required to further quantitatively evaluate the role of biomass burning and heterogeneous uptake in the abundance as well as budget of atmospheric peroxides and facilitate our knowledge of the formation of haze pollution.

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Table 1. Summary of the concentrations of atmospheric peroxides during Wangdu Campaign 2014.

		H ₂ O ₂ (ppbv)	MHP (ppbv)	PAA (ppbv)
	D.L. ^a	0.01	0.01	0.01
24 h	N ^b	1797	1797	1797
	Mean	0.51	0.4716	0.0403
	S.D. ^c	0.90	0.2021	0.11
	Median	0.19	0.11	0.01
	Maximum	11.3	1.25	1.49
Daytime (06:00–18:00 LT ^d)	N ^b	829	829	829
	Mean	0.55	0.16	0.03
	S.D. ^c	0.83	0.4718	0.12
	Median	0.24	0.12	0.01
	Maximum	10.202	1.20	1.49
Nighttime (18:00–06:00 LT ^d)	N ^b	968	968	968
	Mean	0.48	0.17	0.04
	S.D. ^c	0.96	0.23	0.11
	Median	0.15	0.11	0.01
	Maximum	11.333	1.25	1.47

^a D.L.: detection limit.

^b N: number of samples.

^c S.D.: standard deviation.

^d LT: local time.

Table 2. Chemical mechanisms for $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and CH_3O_2 related chemistry modified or added to MCMv3.3.1.

Reactions	Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference
$\text{CH}_3\text{C}(\text{O})\text{O}_2$ chemistry		
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{O}_2$	$2.40 \times 10^{-11} \times 0.37$	Winiberg et al. (2016)
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OH} + \text{O}_3$	$2.40 \times 10^{-11} \times 0.12$	Winiberg et al. (2016)
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{CO}_2 + \text{OH} + \text{O}_2$	$2.40 \times 10^{-11} \times 0.51$	Winiberg et al. (2016)
CH_3O_2 chemistry		
$\text{CH}_3\text{O}_2 + \text{OH} \rightarrow \text{PRODUCT}$	2.80×10^{-10}	Fittschen et al. (2014)

Table 3. Linear regression of atmospheric peroxide species to CO and K⁺ for three biomass burning events during the Phase II (15 June–17 June). Correlation coefficients shown in italic and bold indicate statistical significance ($p < 0.05$) and higher statistical significance ($p < 0.01$), respectively.

Species	Slope ^a	Correlation coefficient		N ^b	Critical correlation coefficient
		CO	K ⁺		
<i>Event I</i>					
H ₂ O ₂	2.17×10^{-3}	0.8144	0.8432	10	0.7646 ($p < 0.01$), 0.6319 ($p < 0.05$)
MHP	1.23×10^{-3}	<i>0.6873</i>	<i>0.7624</i>	10	
PAA	7.16×10^{-4}	0.8378	0.9515	10	
<i>Event II</i>					
H ₂ O ₂	1.32×10^{-3} ² N/A ^c	0.9134 <i>A^c</i>	0.85389394 <i>++12</i>		0.73487079 ($p < 0.01$), 0.60215760 ($p < 0.05$)
MHP	2.30×10^{-3} ³ N/A ^c	0.8876 <i>A^c</i>	0.70429491 <i>++12</i>		
PAA	6.73×10^{-4} ⁴ N/A ^c	0.8399 <i>A^c</i>	0.53309449 <i>++12</i>		
<i>Event III</i>					
H ₂ O ₂	N/A ^c	N/A ^c	0.9632	9	0.7977 ($p < 0.01$), 0.6664 ($p < 0.05$)
MHP	N/A ^c	N/A ^c	0.8741	9	
PAA	N/A ^c	N/A ^c	0.8436	9	

^a Slope: enhancement ratio of speciated peroxides relative to CO.

^b N: number of samples.

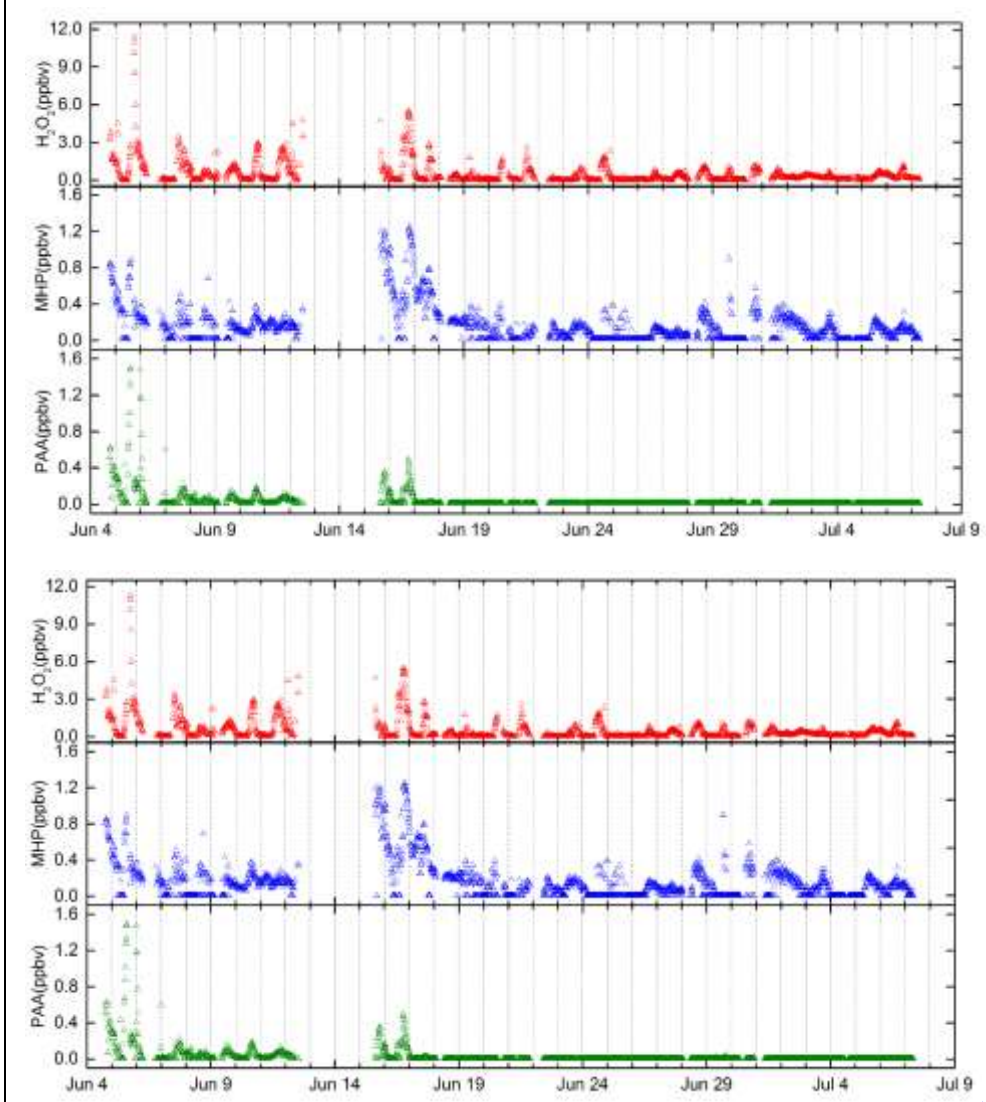
^c N/A: missing data.

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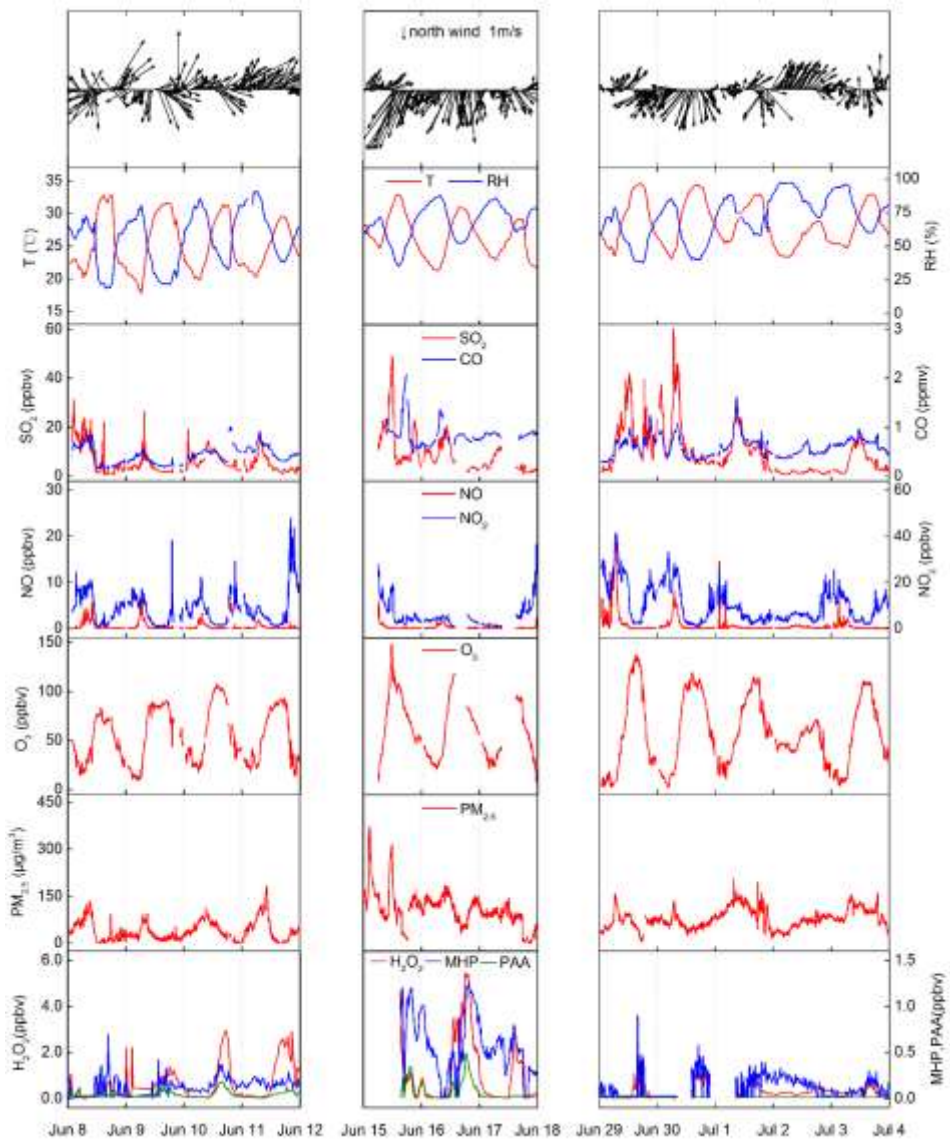
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Figure 1. Temporal profile for atmospheric peroxides over the entire Wangdu Campaign 2014.



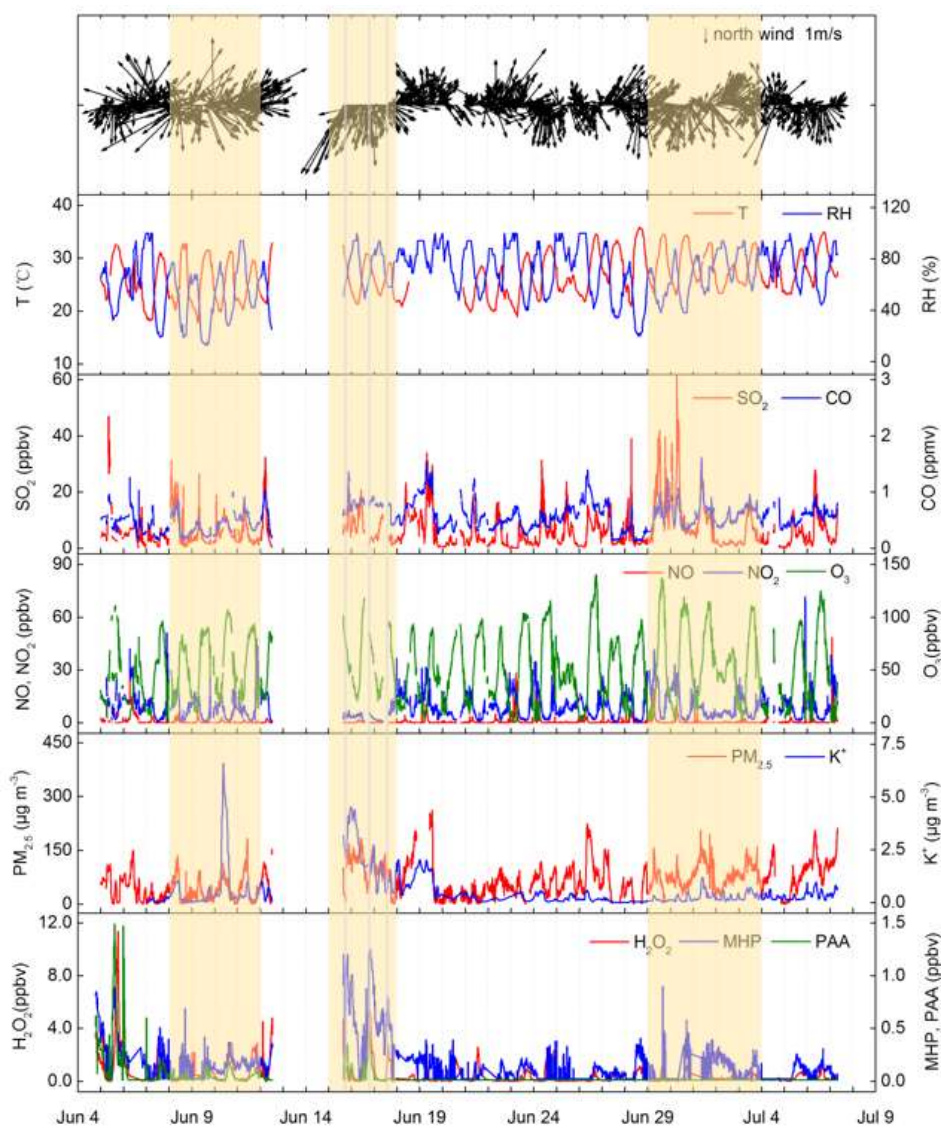


Figure 2. Time series of meteorological parameters, chemical species and atmospheric peroxides for. The orange shade represents the Phase I (8 June–11 June), Phase II (15 June–17 June) and Phase III (29 June–3 July). The grey shade indicates three biomass burning events.

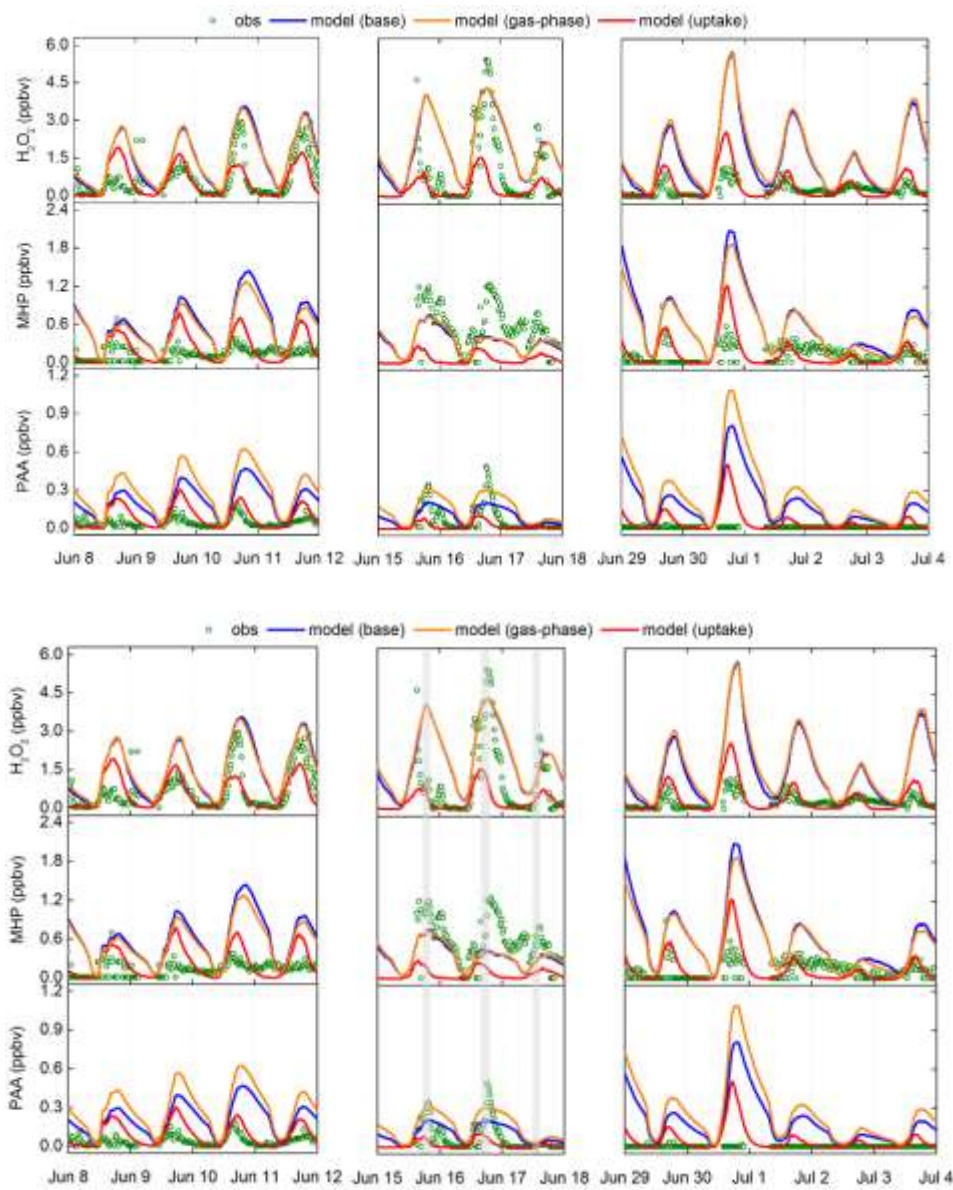


Figure 3. Observed and modelled concentrations of atmospheric peroxides for Phase I (8 June–11 June), Phase II (15 June–17 June) and Phase III (29 June–3 July). The green circles represent observed concentrations. The blue, orange and red lines indicate the modelled concentrations from three different scenarios: base case, new gas-phase reaction case and heterogeneous uptake case, respectively. [The grey shade indicates three biomass burning events.](#)

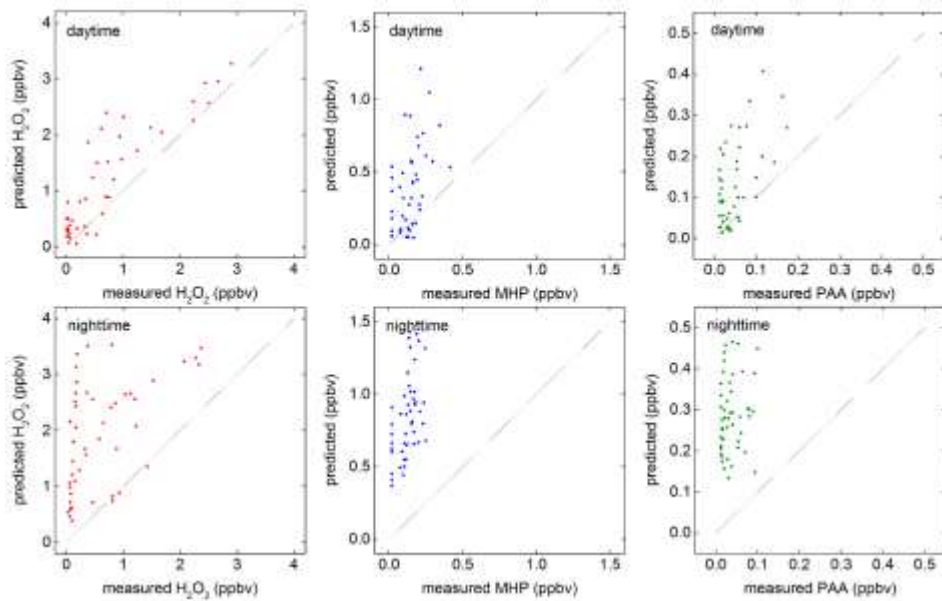


Figure 4. Comparisons between measured and predicted concentrations of atmospheric peroxides [in the model base case](#) for daytime and nighttime during the Phase I (8 June–11 June). The solid lines represent the 1:1 ratio of observed to modelled values.

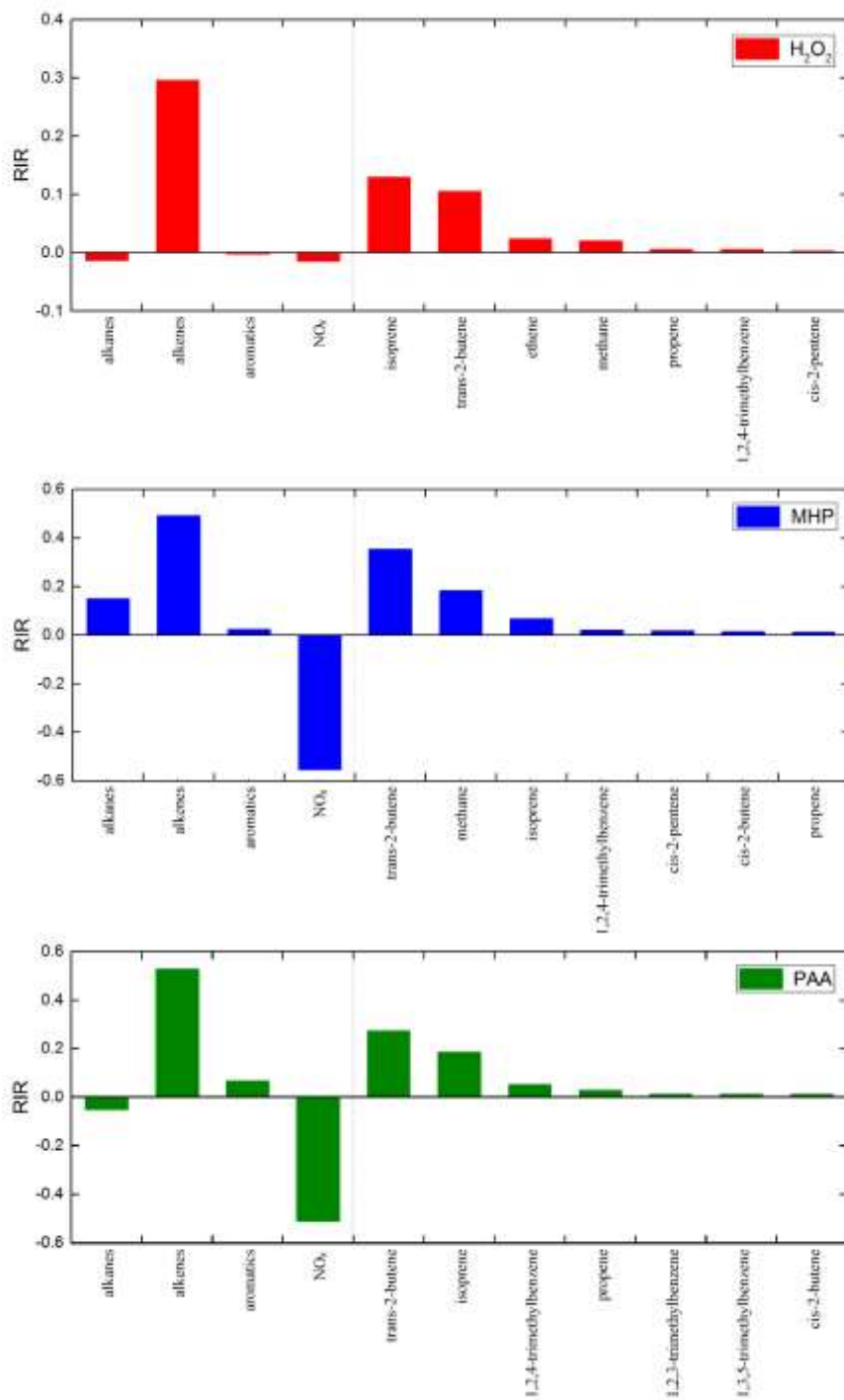


Figure 5. Sensitivity of production rate of atmospheric peroxides to major VOC precursor groups and individual VOC species for Phase I and Phase III.

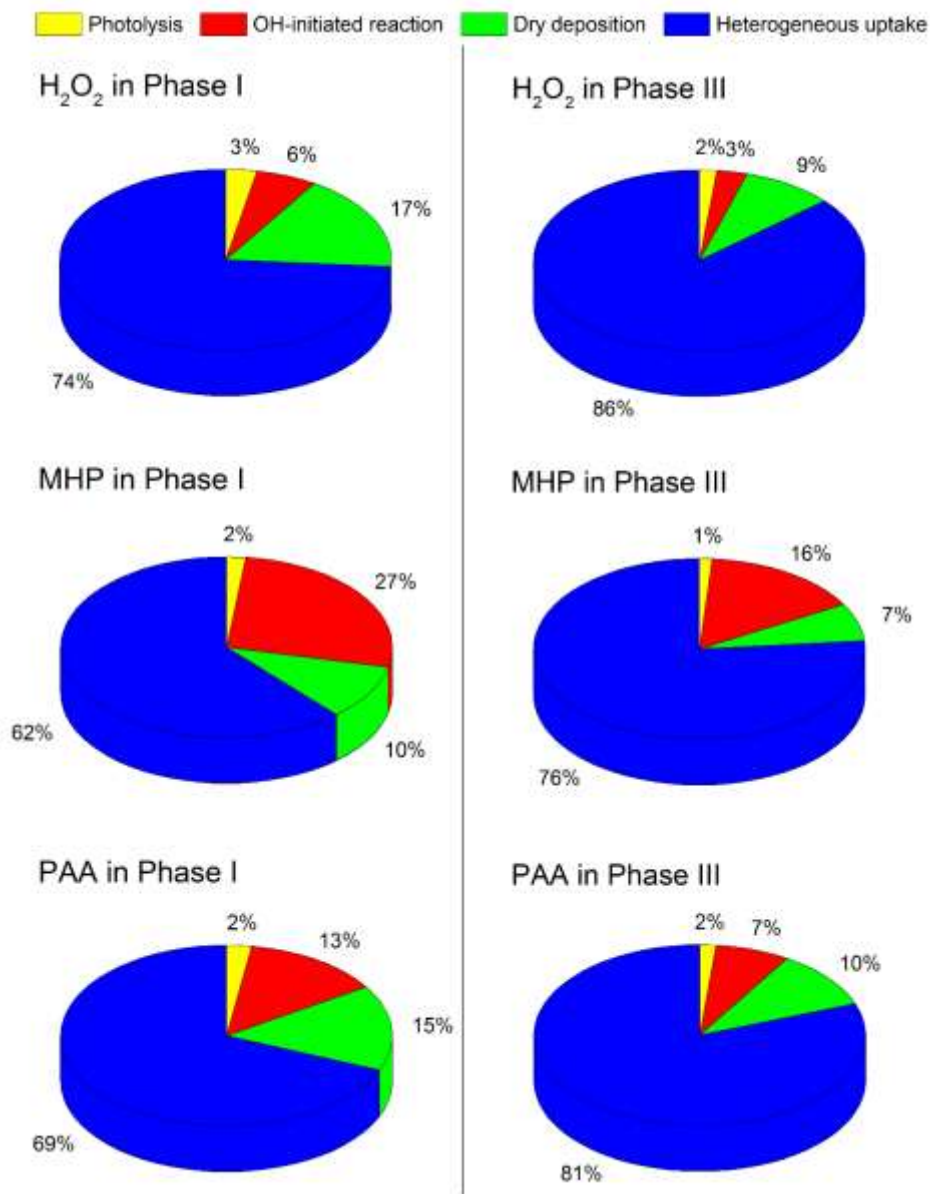


Figure 6. Contributions of each sink to H₂O₂, MHP and PAA destruction in the box model with the heterogeneous uptake by aerosols added during Phase I and Phase III.