Response to the comments of referee #1:

We thank the reviewer for their helpful comments. The referee's comments are first given in black type, followed by our response to each in turn in blue type. Any changes to the manuscript in response to the comments are then given in quotation marks in red type and the line number isin the Microsoft-word version of revised MS without revision. The line number may be different in the PDF version, so please see the section number mentioned in the Response. Figure Response 1 and Figure Response 2 only appear in the Responses and not the revised MS, in order to illustrate the responses to the referee comments. We have now added D. Moon, M. Baeza-Romero and D. Heard as co-authors to this paper since their unpublished experimental data have been included in this paper and they have contributed to enhance the manuscript.

Comment:

1. Please clarify how the ionic strength in Equation 4 is calculated. Is this calculated in the MARK model and what would a typical value be?

Response:

The ionic strength (I, mol L^{-1}), is calculated in the model via Equation 8 in section 2.2.2 on line 124. Typical values for I are in the range of $2.16 - 17.75$ mol L^{-1} based on the ion concentrations in the aerosol bulk and the RH ranging from 40% - 90%.

Comment:

2. For all tables please add units where these are missing.

Response:

We added the units in Table 2, 3, 4 and 5 which is now Table S. 1, S. 2, S. 3, and S. 4 in the Supplementary Information of the revised MS.

Comment:

3. In Table 4 what are the values of k_{mt} or how are these calculated?

Response:

We added more information about the definition and importance of k_{mt} in part 2.1 on line 78 around Equation (3):

"An approach to combine both gas phase molecular diffusion and liquid phase interface mass transport processes is through one variable called k_{mt} (Schwartz, 1984;Schwartz, 1986), which is used in the calculation for gas-liquid multiphase reactions in many modelling studies (Lelieveld and Crutzen, 1991;Chameides and Stelson, 1992;Sander, 1999;Hanson et al., 1994). The definition of k_{mt} is:

$$k_{mt} = \left(\frac{R_d^2}{3D_g} + \frac{4R_d}{3v_{HO_2}\alpha}\right)^{-1} \tag{3}$$

k_{mt} is used to connect the gas phase reactions and the aerosol condensed phase reactions. The rate of gas phase reactants (X) diffusing and dissolving to the condensed phase can be calculated in the framework of aqueous phase reactions as $k_{mt\_X} \times$

35     $ALWC$ (where X is the reactant molecule). Moreover, the conversion rate of aqueous phase reactants to gas phase can be calculated as $\frac{k_{mt\_X}}{H^{cc} \times RT}$ where H^{cc} is the effective Henry's law constant [M atm^{-1}]. The unit of k_{mt} is s^{-1}, as k_{mt} contains the conversion from m$_{air}^{-3}$ of the gas phase molecule concentrations to m$_{aq}^{-3}$ of the aqueous phase molecule concentrations and backward. For larger particles (radius >1 μm), k_{mt} is mainly determined by gas phase diffusion of HO$_2$. For smaller particles (radius <1 μm) k_{mt} is mainly determined by the accommodation coefficient (α). The MARK model can simultaneously

40   simulate gas and liquid two-phase reaction systems in the same framework."

The typical value of k_{mt} of HO$_2$ for small particles with the radius of 50 nm is 3.85×10^5 s^{-1}, and for larger particles with the radius of 1 μm is 1.93×10^4 s^{-1}.

Comment:

45   4. Are all reactions in the tables included in the model? If so how does this relate to keff in Equation 11?

Response: All reactions in the tables are included in the model. k_{eff} is the comprehensive reaction rate coefficient encompasses both HO$_2$ dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO$_2$ uptake process. k_{eff} is mostly affected by the concentration of copper, the HO$_2$/O$_2^-$ cycle in the liquid phase and HO$_2$ dissolution equilibrium. HO$_2$/O$_2^-$ reacting with Cu ions (R 1, R 2, R 8 and R 9) may directly affect k_{eff} thus change the model result of

50   γ_{HO_2}. OH$_{(aq)}$, O$_{2(aq)}$, O$_{3(aq)}$, H$_2$O$_{2(aq)}$ will also influence the reaction system because they have direct relationship with the dissolution equilibrium and reactions of HO$_2$, O$_2$, H$_2$O$_2$ OH and O$_3$. H$_2$O$_2$ is also a reaction product of HO$_2$/O$_2^-$ reacting with Cu ions, its concentration will also affect the reaction system. Sulfate ion, ammonium ion and nitrate ion may not directly affect the system, while they will change the concentration of aqueous HO$_2$, O$_2$, H$_2$O$_2$, OH, O$_3$ and their solubility. What ismore, HO$_2$ uptake process may influence the oxidation rate of SO$_2$ and other reagents, to which more research is needed.

55

Comment:

5. It's stated that in the model it is assumed that the surface concentration and the bulk concentration equal each other. It is also stated that this is only valid for particles with a radius less than 200 nm. However, the model and resulting parameterization are then applied to particles which are larger than this and many particles in the atmosphere are larger than this. I wonder why

60   the authors don't seem to have used the correction in equations 10 and 11 and what impact this will have on their final results and the applicability of their parameterization to future studies?

Response:

The size of the particles is an important factor within the MARK model when considering gas phase diffusion to the particle surface and HO$_2$ desorption. While the HO$_2$ radical concentration is not a factor that influence γ_{HO_2} in the MARK model.

65 In ambient urban situations, the Count Median Diameter (R_d) of aerosol particles is smaller than 1 μm in most instances. The ratio of $\overline{[HO_2]}$ to $[HO_{2(r)}]$ is 0.89 calculated by the MARK model simulation of k_{eff} with a RH 40%-90%, the copper ion concentration varies from 10^{-5} to 1M at 1 μm diameter particles. The ratio will be even higher and close to 1 with smaller particles (>0.95 at 400 nm diameter). The MARK model is valid for particles with R_d smaller than 400 nm and may cause small deviations for particles with R_d smaller than 1 μm. Thus, in this paper, we assume the surface concentration of HO_2 equals

70 to the condensed phase average HO_2 concentration.

A model considering the influences of aerosol particle size distribution and HO_2 concentration gradients on γ_{HO_2} is currently under development.

We changed the statement in the origin MS in part 2.2.3 on line 148 and modified as: "In the copper-doped aerosol particle, because of the high value of k_{eff} and small Count Median Diameter (R_d) (usually smaller than 1 μm), the ratio is close to 1.

75 At a diameter of 1 μm, and a relative humidity between 40% and 90%, the condensed phase copper ion concentration varies from 10^{-5} to 1M, the average ratio of the surface HO_2 concentration and the condensed phase HO_2 concentration is 0.89. At 400nm diameter particles for $RH = 40\%$ to 90%, the ratio is larger than 0.95. The ratios are calculated by simulation of k_{eff} and the accordingly calculations by Equation (12) and (13)."

80 Comment:

6. In Figure 2 what is the main cause for the decrease in the uptake coefficients between the original parameterization and the new model results. Is the difference mainly due to the different rate coefficient being used, the use of activity coefficients or something else?

Response:

85 The parameterization proposed by the IUPAC uses only one rate constant as the second-order reaction rate k^{II} of Cu^{2+} and HO_2. We use 1.5×10^7 L mol^{-1} s^{-1} as the secondary reaction rate k^{II} rather than the more commonly used value of 1×10^9 L $mol^{-1}s^{-1}$ in the calculation of the original parameterization.

We added the reason of using 1.5×10^7 L mol^{-1} s^{-1} in the calculation in the revised MS in Section 3.2 on line 241:

"The prior value (1.5×10^7 M^{-1} s^{-1}) reflects the rate of reaction between HO_2 and Cu^{2+}, more prevalent in acidic aerosol such

90 as ammonium sulphate, and the latter between O_2^- and Cu^{2+} ions, which is more prevalent in aerosols with a pH greater than the pK_a of HO_2, such as NaCl (Bielski et al., 1985). This treatment within the calculation can bring predictions more in line with experimental results (Figure 2 grey dotted line) compared to the high value of 1×10^9 L $mol^{-1}s^{-1}$ used in the existing parameterized equation."

And on line 256 the main reason of the differences between original parameterization and the MARK model:

95 "The main reason for the differences between the original parameterization and the MARK model is the effect of including the activity coefficients of Cu ion and HO2 and the effects of reactions of different valence states of copper ions."

7. For Figure 2 what is the aerosol pH and how is it calculated?

Response:

The main components of the aerosols used in the laboratory measurements of γ_{HO_2} shown in Figure 2 are ammonium sulfate and a small amount of copper sulfate. According to the calculation based on the aqion 7.0.8 interface (for details please see https://www.aqion.de/), the pH is around 4.54 considering aerosol dehydration with 2M aerosol bulk sulfate concentration and 1M Cu ion at 25 ℃. In the MARK model, we set aerosol pH as 4.5 when compared to the laboratory results. We have re-calculated γ_{HO_2} at pH=4.5 and added data points from Lakey et al., JPCA (2016) based on the short comments from Pro. Heard. In the revised MS, Figure 2 is modified as follows:
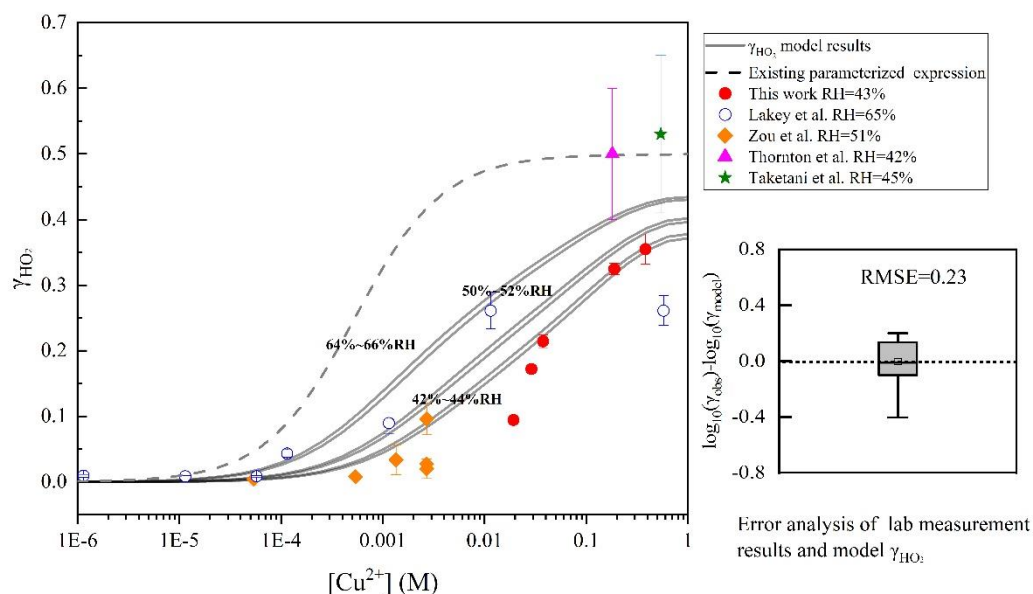
"Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red filled circles denote the results at 43% *RH* measured at Leeds. Blue hollow circles at 65% *RH* (Lakey et al., 2016). Yellow filled diamonds denote results at 51% *RH* (Zou et al., 2019), filled purple triangle at 42% *RH* (Thornton and Abbatt, 2005)) and filled green star at 45% *RH* (Taketani et al., 2008)). The grey dotted line denotes the current parameterized equation (Thornton et al., 2008;Hanson et al., 1992;Hanson et al., 1994;Jacob, 2000;Kolb et al., 1995) and the solid grey lines represent the model results of MARK model in this study at various *RH*. The root mean square error (RMSE) between the MARK modelled values and the full dataset (0.23). Aerosol pH is set as 4.5 based on aqion 7.0.8 interface considering the participation of Cu ion (for details please see https://www.aqion.de/)."

Comment:

8. Figure 2 seems to be missing some previously published data point(s) from Lakey et al., JPCA (2016). It seems that the point at the highest copper concentration in that work (which is not shown in Figure 2) would not fit the modeled line. The authors should include any previously published missing points for completeness. Are they able to model or at least speculate as to why this data point does not fit their model.

Response:

We have now added these data points from Lakey et al., JPCA (2016) at the highest and the lowest copper concentration used to Figure 2 for completeness. Please also see the response to the Short Comment from Professor Heard, University of Leeds. Prof. Heard, Dr. Moon and Dr. M. Baeza-Romero from Leeds are now added as co-authors to the paper, with the correct data from Lakey et al., (2016) used for *RH*=65% and from the PhD thesis of Dr. Moon for *RH*=43% included. Moreover, in order to model the results from Lakey et al., JPCA (2016), we change the accommodation coefficient to 0.26 in the MARK model as they recommended in the paper, and get the result as follows:
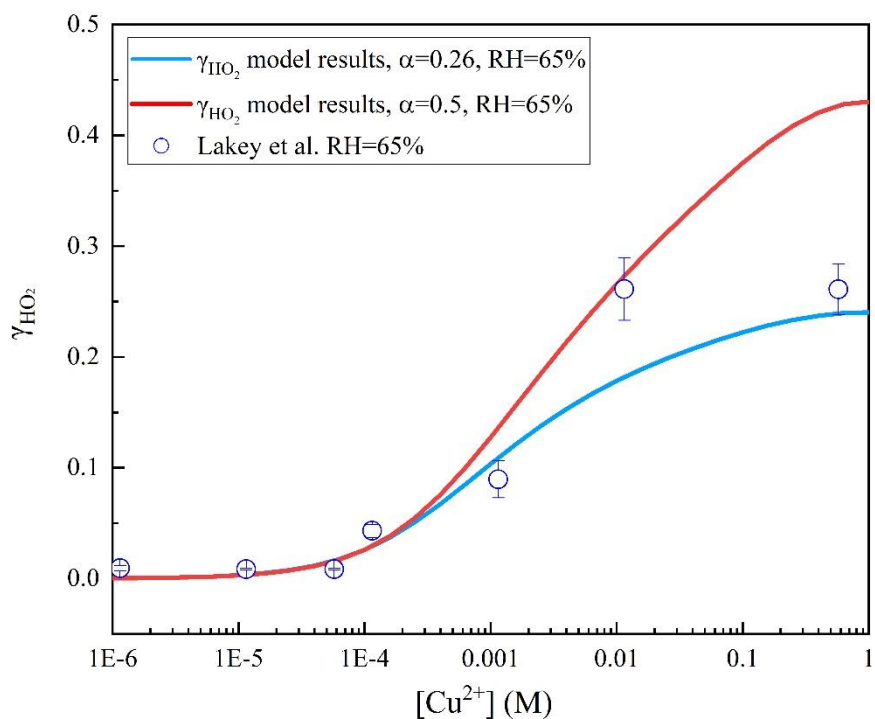
Figure Response. 1 Comparison of the dependence of γ_{HO_2} on aerosol copper ion concentration with α_{HO_2} as 0.26 and 0.5 at 65% *RH*. The solid line denotes the MARK model results, and the blue hollow circles denote the results at 65% *RH* measured by Lakey et al. (2016).

Model results using α_{HO_2} as 0.5 fits well with the results from Lakey et al. (2016) when [Cu^{2+}] smaller than 0.1M while have larger deviation for higher [Cu^{2+}]. α_{HO_2} as 0.26 fits unsatisfactorily at [Cu^{2+}] around 0.01M. Considering the ambient aerosol condensed phase [Cu^{2+}] (for example, ranging from 0.003 to 0.012 M in Wangdu campaign), in this MS we still use α_{HO_2} as 0.5 to get the novel HO_2 uptake parametrization.

The accommodation coefficient may change in the process of the experiments for some reasons. For example, the reaction time and HO_2 initial concentration (see next comment by the reviewer). Aerosol phase state is also an important factor influenced α_{HO_2}. Moreover, during the efflorescence of aerosol particles in drying nafion tube, different concentrations of copper ions may have a certain effect on particle phase state which will influence α_{HO_2}. This part should be further studied.

9. George et al. PCCP (2013) noticed higher uptake coefficients for lower HO_2 concentrations for copper doped particles. Did the authors do any sensitivity tests with different HO_2 concentrations and do they see any difference?

Response:

The γ_{HO_2} measured in the flow tube experiments indeed depends both on the HO_2 concentration and also the reaction time between HO_2 and the aerosols.. However, sensitivity tests in the MARK model show no γ_{HO_2} decreasing trend with increasing [HO_2]$_0$ in the absence of Cu ions, and γ_{HO_2} will slightly increase with the [HO_2]$_0$ in the presence of Cu ions in the MARK model.

A possible explanation for the results from George et al. PCCP (2013) could be the Fenton-like reactions of Cu ions and H_2O_2 that is an additional source of HO_2. More H_2O_2 will be generated with greater light intensity and may accumulate along the flow tube with the reaction of HO_2 with aerosol for H_2O_2 is one product of HO_2 uptake. However, H_2O_2 and Cu ions reactions need to be of the same order of magnitude or no more than one magnitude lower than that of HO_2 reaction with Cu ions to make obvious differences in the measurement of γ_{HO_2}. In the MARK model, H_2O_2 only reacts with Cu^+ and the reaction rate constant is 7×10^3 L mol^{-1} s^{-1} which is too small to influence γ_{HO_2} with the changes of H_2O_2 concentration, and so it may explain the lack of sensitivity of the uptake coefficient with HO_2 concentration.

10. Figure 3: Is lg on y axis log10?

11. Figure 3: Please explain this figure in a more detailed fashion. It is unclear to me what the markers are and why there is a range of values. Why does there seem to be a larger difference between the model and the parameterization at low relative humidity?

Response:

We have changed the y-axis label in accordance with the referee ́s comment in Figure 3 in the revised MS. We calculated the RMSE of γ_{HO_2} predicted by MARK and the corresponding calculated values from the new parameterized equation at different *RH* and Cu ion concentrations.

We added the explanation of the larger difference between the model and the parameterization at low relative humidity in line 290 on the second last paragraph of section 3.3 in the revised MS:

"The range of values shows the difference between the modeled data and parameterized equation data at different Cu concentration. At low *RH* and consequently relatively low ALWC, γ_{HO_2} is more sensitive to [Cu^{2+}] expecially at low [Cu^{2+}]

170   ($<10^{-4}$M). This sensitivity can not be fully represented in the parameterized equation. What is more, at low [Cu^{2+}] and low *RH*,

the value of γ_{HO_2} is smaller than in other conditions, small changes of γ_{HO_2} will cause larger RMSE values. "

Comment：

12. Figure 4: Is the data shown measurements or a simulation?

175   13. Figure 5: This figure is not mentioned at all in the text and as such I don't know what the difference is between Figures 4

and 5.

14. Why not combine Figures 4 and 5 for better comparisons?

Response：

Figure S. 1 shows the averaged particle surface-area size distribution (PSASD) and the particle number size distribution (PNSD)

180   of aerosol measured in the Wangdu field campaign. We deleted Figure 5 in the original MS because the information of aerosol

size distribution is redundant. In the SI of the revised MS, we have added Figure S.1 as follows:
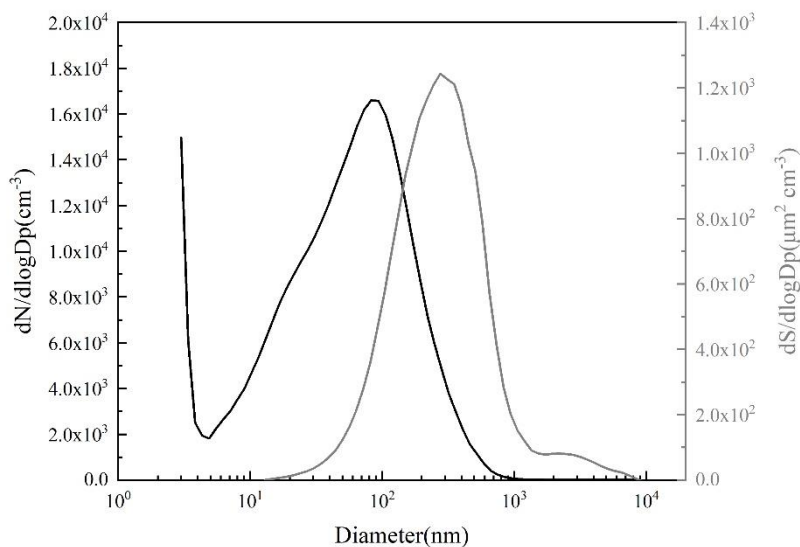

Figure S.1: The dry-state particle number size distribution (PNSD) (black line) and particle surface-area size distribution

(PSASD) (grey line) of aerosol for conditions encountered during the Wangdu field campaign.

185

15. Can the authors speculate as to why the HO_2 uptake coefficient is higher at night (Figure 6)?

Response:

We add the table below in the SI for revised MS as Table S. 5. Table S.5 shows the median and average values of the copper

concentration, PM loading and *RH* during the day and at night. During the day the copper concentration is larger, but the lower

190   *RH* may limit γ_{HO_2}. Thus, k_{het}, the quasi-first order reaction rate constant of HO_2 heterogeneous uptake is slightly higher at night compared to the daytime, contributing to the higher γ_{HO_2} predicted at night.

Table S.5. The median and average values used in the calculation of γ_{HO_2} in Wangdu

	Value	Cu [ng/m^3]	PM$_{2.5}$ mass [µg/m^3]	*RH* [%]	γ_{HO_2}	k_{het}[s^{-1}]
Day	median	33.42	77.9	55.4	0.119	0.017
	average	44.66	85.0	57.6	0.126	0.020
Night	median	19.01	70.6	68.9	0.134	0.021
	average	34.16	67.9	67.4	0.147	0.023

195

16. In Figure 6 what is the main cause of the distribution in HO_2 uptake coefficients? Is it due to different copper concentrations in the particles or something else?

Response:

The distribution of γ_{HO_2} is mainly due to the different copper concentrations and ambient *RH*. Although the PM mass is also

200   a parameter in the empirical equation proposed by this MS, it shows small partial correlation on γ_{HO_2}. Figure S 2 below shows the partial correlation coefficient between γ_{HO_2}, field measured [HO_2], [OH], $TR_{HO2uptake}$ and R_1 with aerosol mass loading in Wangdu campaign. This figure is now added in the SI of the revised MS.
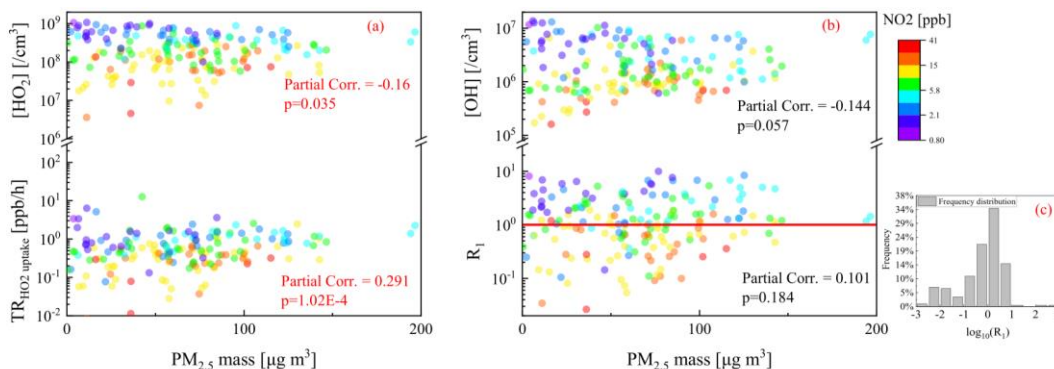
"Figure S.2. Impact of the HO_2 uptake evaluated with the novel empirical equation for conditions encountered during the

205   Wangdu field campaign. Partial correlation of logarithmic values of $TR_{HO2uptake}$ and R_1 with respect to aerosol loading were calculated. The partial correlation coefficient in panel (a) means that $TR_{HO2uptake}$ has a small partial correlation with aerosol loading. No partial correlation of R_1, [HO_2] and [OH] to aerosol loading is observed. The different coloured dots show different [NO_2]. Panel (c) is the distribution of $log_{10}R_1$."

210

17. Were any HO$_2$ measurements made during the Wangdu field campaign and if so was any box modeling of the Wangdu campaign performed to determine whether there was a discrepency between measured and modeled HO2 uptake coefficients? Were predicted HO2 uptake coefficients in the range that was expected? If no HO2 measurements were made, could the authors clarify why they chose this particular field campaign to apply their model to?

215   Response:

Yes, HO$_2$ and other radical concentration measurements were made during the comprehensive campaign in Wangdu.

We added the following statements in the revised MS in section 3.4.3 the second paragraph on line 347:

"Tan et al. (2017) had compared the measured and modelled OH, HO$_2$ and RO$_2$ radicals in the Wangdu campaign. However, in this paper, they did not discuss the influence of HO$_2$ uptake. A very recent publication (Tan et al., 2020) calculated γ_{HO_2} in

220   the Wangdu campaign based on the comparison of field measurement data for HO$_2$ and concentrations calculated by the box model. The paper proposes that all γ_{HO_2} calculated in this way from the Wangdu campaign can be fitted to a Gaussian distribution around the value of 0.08 ± 0.13. This value is similar to our estimation in this paper considering the indirect measurement uncertainty (please see the SI)."

225   What is more, we recalculated the ratio ($R1$) of HO$_2$ uptake to ROx termination rate with measured RO$_2$ concentration which is now in consist to the dataset of (Tan et al., 2020). In the original MS, we used the modeled RO$_2$ radical concentrations which is underestimated compared to the measured results. Thus, $R1$ decreases obviously due to the competition of larger proportion of RO$_2$+HO$_2$, RO$_2$+NO and RO$_2$+RO$_2$ reactions in the ROx radical termination budget.

230

18. Line 313: The authors may want to clarify that 'aerosol properties' may include phase state and that previous measurements have shown lower uptake coefficients for semi-solid and solid particles (e.g. Lakey et al. ACP (2016)). The authors should also clarify somewhere that one of the major limitations of their model is that they assume steady-state concentrations and do not consider concentration gradients which will occur and could change over time for semi-solid particles.

235   Response:

We changed the word "properties" as "aerosol particle condensed phase component concentrations" in the revised MS in Part 2.2.2 on line 116 at the first paragraph and Part 3.4 on line 314 at the second paragraph to avoid the inaccurate statement of aerosol properties including phase state that is not considered in the MARK model used in this MS.

240   We added the following statement in the revised MS in section 4 on line 377:

"The novel empirical equation is applicable under the assumption of steady-state concentrations and with metastable or liquid aerosol particles (if the ambient *RH* over a completely liquid aerosol decreases below the deliquescence *RH*, the aerosol may not crystalize immediately but may constitute a supersaturated aqueous solution (i.e., in the metastable state) (Song et al.,

2018)). The approximate calculation of HO_2 concentration gradients within the aerosol particle condensed phase also cause
245 deviations for larger particles. The bulk diffusion coefficient of HO_2 and other reactive molecules should be lower in the situation of semi-solid particles (Berkemeier et al., 2016;Shiraiwa et al., 2010;Mikhailov et al., 2009) and would change with the water activity and the organic components (Price et al., 2015). This aspect needs further studies. For crystalline or amorphous solid aerosol particles, HO_2 will undergo surface reactions and diffuse across the surface rather than be accommodated within the aerosol bulk. The MARK model has limitations in the calculation of γ_{HO_2} with semi-solid aerosol
250 particles. In the Wangdu campaign, κ_{sca} (optical aerosol hygroscopicity parameter) ranges from 0.05 to 0.35 with an average of 0.22. The ambient RH during the Wangdu campaign shows significant diurnal variations and varies greatly from 15% to 97%, with an average value of 61% (Kuang et al., 2019) indicating that the percentage of solid aerosol particles is relatively low and hence do not significantly influence γ_{HO_2}.

"

255

19. The authors fix the solubility of copper at 25%. In reality solubility can vary considerably. How sensitive is this parameter in their model?

Response:

260 The MARK model is sensitive to Cu ion concentrations that exceed 1×10^{-4} M. We tested the sensitivity of soluble copper ion concentration in the Wangdu campaign between the value of 10% to 70% (Fang et al., 2017;Hsu et al., 2004;Hsu et al., 2010). γ_{HO_2} will increase 1.57 times from 0.075±0.031 at 10% solubility to 0.193±0.079 at 70% solubility based on the GaussAmp fitting of data from Wangdu campaign. Even at 70% solubility (which is unlikely true for most situations), the central value of γ_{HO_2} is lower than 0.2. The figure below shows the variation of the uptake coefficient with Cu ion solubility.

10

Wangdu campaign

γ_{HO_2}
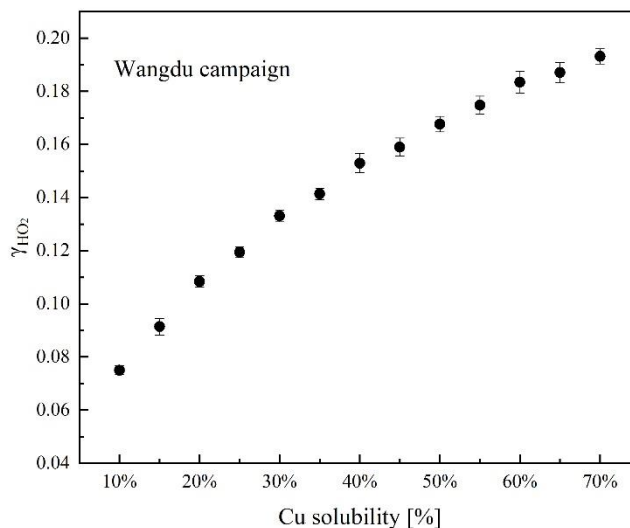
Cu solubility [%]

Figure Response.2 Sensitivity analysis of Cu solubility in the calculation of γ_{HO_2} for conditions encountered during the Wangdu campaign.

In the revised MS part 3.4.2 we discussed the influence factors of Cu solubility in the aerosol.

20. Another limitation of the model is that they don't consider reactions between different metal ions (such as Reaction 4 in Mao et al. ACP (2013)) which they have stated. However, could they also speculate how this could impact the estimated uptake coefficients for atmospheric aerosols (e.g. is it expected that this would increase the uptake coefficient)?

Response:

According to our understanding, there is no direct published laboratory measurement evidence of Cu-Fe redox coupling mechanism in HO$_2$ uptake. We speculate that the upper limitation of γ_{HO_2} may not change because of the low solubility of Fe and the influence of organic matters. However, whether the product of HO$_2$ uptake is H$_2$O$_2$ or H$_2$O will affect atmospheric oxidation capacity, as outlined by Mao et all (Mao et al., 2013). This should be studied in the future. In the revised MS Section 4, we discussed the influence of other TMI on γ_{HO_2}.

21. Please check the references carefully as many seem to wrong (e.g. Schwartz and Meyer 1986 line 108 and references in Figure 2).

Response:

We have checked the references in the updated manuscript, and the references in Figure 2 are also checked based on the Short Comment from Professor Heard (please see the first short comment). On line 43 in Section 1, line 79 in Section 2.1, line 142 in Section 2.2.3 and line 263 in Section 3.3, we changed the reference as Schwartz (1984) and Schwartz (1986). Moreover, we

removed inaccurate references on line 33, 206 in the original MS and in Table S.3 and part S.1 in the revised MS. We also checked the references for the misuse of capitalization and subscripting.

290

Response to the comments of referee #2

We thank the reviewer for their helpful comments. The referee's comments are first given in black type, followed by our
295 response to each in turn in blue type. Any changes to the manuscript in response to the comments are then given in quotation marks in red type and the line number is in the Microsoft-word version of revised MS without revision. The line number may be different in the PDF version, so please see the section number mentioned in the Response.

We have now added D. Moon, M. Baeza-Romero and D. Heard as co-authors to this paper since their unpublished experimental data have been included in this paper and they have contributed to enhance the manuscript.

300

In summary, the comments made by the referee and our responses to them can be classified into the following categories:

1 The comparison of the results from the empirical equation proposed here with the existing parameterization proposed by IUPAC.

305 2 Discussion of the influence of the organic content of particles.

3 Correction of different definitions of the same terms and the obscure statements.

4 The corrections of citations in the manuscript.

5 Responses to other specific points.

6 Explanation of part of the SI

310

Comments are numbered for categorization. For example, 1.1 refers to the first comment in the first category above.

The manuscript of Song et al deals with an important theme in atmospheric science; the interaction of HO_2 with particles containing dissolved copper and the modelling of the impact of this heterogeneous reaction on e.g. O_3 production.

315 We thank the reviewer for recognising this.

1.1 Song et al have analysed laboratory data and derived an empirical expression that they then implemented in a model. They suggest that their parameterisation is superior to taking a constant value of 0.2 for the uptake coefficient. This is most likely true but why do they not compare to other parameterisations of this process, e.g. that proposed by IUPAC which also considers

laboratory studies up to 2016 and which has a physical basis (i.e. aqueous phase rate coefficients for reaction of HO_2/O_2^- with Cu).

In the original manuscript Figure 2, we compared the novel empirical expression to parameterizations proposed by IUPAC, however we did not include this reference and we simply called it the Resistance Model. In the revised manuscript section 3.2 beginning (line 212), we referred to the sources of the existing parameterization as "(Thornton et al., 2008;Hanson et al., 1992;Hanson et al., 1994;Jacob, 2000;Kolb et al., 1995;Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.)".

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2.1 They also do not consider in any detail the potential for organic content of particles to reduce the uptake coefficient considerably as this is mentioned only in passing on line 312-315. Thus aspect will be central to improving the modelling of HO_2 uptake to particle matter, as has been shown e.g. for N_2O_5. The sentence on line 149-150 in this regard is highly misleading: "Without the interference of organic matter, it is convenient to explore the mechanism of HO_2 heterogeneous uptake and derive its parameterized equation, which provides a good reference for the heterogeneous uptake of HO_2 in the actual atmosphere environment". The co-authors from Jülich will be intimately familiar with this aspect of heterogeneous chemistry and should be able to provide input.

We agree that this sentence is misleading, and whilst recognising that the model has considerable uncertainties, we feel that extending the current IUPAC parameterisation to include the concentration of Cu^{2+} ions (measurements of which in aerosol are available from the field) represents an advance. We have changed the relevant text on line 176 in section 3.1 the first paragraph as follows in the revised MS:

"A simplified approach was used to explore the mechanism of HO_2 heterogeneous uptake in order to derive a parameterized equation for the uptake coefficient, γ_{HO_2}, and which did not consider any potential role of organic matter present in the aerosol because of the reasons detailed below.

Using laboratory measurements of γ_{HO_2} for particles containing a single organic component (Lakey et al., 2016;Lakey et al., 2015), it was concluded that the organic content of an aerosol particle may affect several important parameters in the model. For example, the aerosol pH, hygroscopic properties of the aerosol, the rate of diffusion of HO_2 within the aerosol and a reduction in the concentration of Cu^{2+} via the formation of complexes that could affect the ability of Cu to undergo redox reactions with HO_2 and O_2^-. Hence, it is expected that the presence of organic material would change the value of γ_{HO_2}, but incorporation of terms in the parameterisation of γ_{HO_2} from organic material is beyond the scope of this work, and should be a focus of future studies. In fact, during a recent field measurement of the urban atmosphere using a combined laser-flash photolysis and laser-induced fluorescence (LFP-LIF) technique coupled with a versatile aerosol concentration enrichment system (VACES) in Japan, Zhou et al. showed that the average value of γ_{HO_2} was 0.24 ± 0.20 (1σ) during the study period (Zhou et al., 2020). Although conditions will be different between field locations, this "field measured" value is within the broad range of our model output that does not include organic matter effects."

13

3.1 The manuscript is illogically organised and difficult to follow, has different definitions of the same term, poor language quality and…

In the revised MS we have tried to improve the language and to be consistent with definitions. Moreover, the revised manuscript is reorganized now according to the following outline:

Abstract

1 Introduction

2 Materials and Methods

  2.1 The Model

  2.2 Corrections on γ_{HO_2} in the MARK model

    2.2.1 Henry's law of gas phase reactants

    2.2.2 Aerosol particle condensed phase Cu^{2+} molality calculation

    2.2.3 The conversion formula of $[\overline{HO_2}]$ and $[HO_{2(r)}]$

  2.3 Laboratory results for the HO_2 accommodation coefficient

3 Results and Discussion

  3.1 Parameter sensitivity analysis of the MARK model

  3.2 Model Validation

  3.3 A novel parameterized equation of γ_{HO_2}

  3.4 Evaluation of the impact of the new HO_2 uptake parametrization in the Wangdu campaign

    3.4.1 Average results of observed meteorological parameters and trace gases concentration in Wangdu campaign

    3.4.2 Calculation of soluble copper ion concentration

    3.4.3 γ_{HO_2} estimated at Wangdu field campaign

4 Summary and conclusions

Author Contribution

Competing Interest

Data Availability

Acknowledgments

References

In order to remove unnecessary details, and to facilitate the flow and aid navigation of the main paper, there is now a supplement with Supplementary Information for the revised MS, which is organised as follows:

S1 Reaction mechanism and reaction rate constants

14

S2 Calculation of aerosol liquid water content (ALWC) and other important parameters for conditions encountered during the Wangdu campaign

S3 The uncertainty of the calculation for conditions encountered during the Wangdu campaign

We also added the forward and backward reaction rate constants in Table S. 2 in the MARK model calculation.

390   Please see the SI for more details.

4.1…incorrectly cites the published datasets of Lakey et al (2016) (see author comment from D. Heard). This work might be publishable after major revision and reorganisation.

In response to the Short Comment from Professor D. Heard, and in consultation with the Leeds group, we have modified the

395   way the data are presented in the Table and Figure (there were some mistakes and incorrect citations were used). The citations in the revised MS have been corrected based on the short comment of Professor D. Heard (please see also the response to the first short comment).

Some specific points are listed below:

400   3.2 L11 hydroxyl peroxy radicals = hydroperoxyl radicals

L12 gamma_HO2 is defined but the expression after line 17 simply lists gamma.

In the new version it has been taken care that only "hydroperoxyl radicals" is used. We changed the wording in the abstract and line 34 in the Introduction.

405   3.3 L15 parameterisation of HO_2? Presumably of HO_2 uptake

On line 21 in the Abstract we have added the word "uptake" in the revised MS.

3.4 Does it make sense to list the expression in the abstract, where none of the terms (e.g. ALWC, [PM], Rd) involved are defined

410   We changed the abstract in the revised MS including the definition of the main parameters of the parametrization as follows: "Heterogeneous uptake of hydroperoxyl radicals (HO_2) onto aerosols has been proposed to be a significant sink of HOx and hence the atmospheric oxidation capacity. Accurate calculation of the HO_2 uptake coefficient γ_{HO_2} is key to quantifying the potential impact of this atmospheric process. Laboratory studies show that γ_{HO_2} can vary by orders of magnitude due to changes in aerosol properties, especially aerosol soluble copper (Cu) and aerosol liquid water content (ALWC). In this study

415   we present a state-of-the-art model to simulate both gas and aerosol phase chemistry for the uptake of HO_2 onto Cu-doped aerosols. Moreover, a novel parameterization of HO_2 uptake was developed that considers changes in relative humidity (*RH*) and condensed phase Cu ion concentrations and which is based on a model optimization using previously published laboratory and new laboratory data included in this workdata. The new parameterization is as follows:

15

$$\frac{1}{\gamma_{HO_2}} = \frac{1}{\alpha} + \frac{3 \times \upsilon_{HO_2}}{4 \times 10^6 \times R_d H_{corr} RT \times (5.87 + 3.2 \times \ln(\text{ALWC}/[\text{PM}] + 0.067)) \times [\text{PM}]^{-0.2} \times [Cu^{2+}]^{0.65}}$$

where α is the mass accommodation coefficients which is the probability that a gas-phase molecule colliding with the aerosol surface leads to dissolution, reaction or volatilization, υ_{HO_2} is the mean molecular speed of HO_2 [cm s^{-1}]. R_d is the Count Median Radius of the aerosols [cm], H_{corr} is the Henry's constant [mol cm^{-3} atm^{-1}] corrected by solution pH ($H_{corr} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right)$, where H_0 is the physical Henry's law constant), R is the gas constant [cm^3 atm K^{-1} mol^{-1}], T is the temperature [K] and [PM] is the mass concentration of particles [μg m^{-3}]. According to the new equation, highly variable HO_2 uptake coefficients (median value ~0.1) were obtained for the North China Plain and the impact of HO_2 uptake on the ROx (=OH + HO_2 + RO_2) budget was assessed."

3.5 L39-40 Meaning obscure. I think the authors refer to the reduction of aerosol mass over the last few years. The information that the uptake coefficient used (in calculating surface ozone) was 0.2 is superfluous here.

We mean that the role of the reduction of HO_2 uptake on aerosol toward that of O_3 production is also dependent on the selection of the HO_2 uptake coefficient, as well as the reduction of aerosol mass itself. We try to modify the text to become clearer as follows,

"… the reduced HO_2 uptake owing to reduction of aerosol surface area is considered to be the key reason for the increased surface ozone concentration over the last few years when a value of 0.2 was used for γ_{HO_2}."

3.6 L57 L is defined as the aerosol liquid water content. In the abstract it is ALWC.

We have changed all usages of L to ALWC. L has the same meaning as the aerosol liquid water content.

3.7 L68 MARKM model is otherwise referred to as MARK

The name of the model is the "MARK" model, we have been careful now to use "MARK" in the revised MS. We corrected "MARKM" to "MARK" on Section 2.2 header and the first paragraph in the SI Section S1.

3.8 L74 Equilibrium constant have capital "K". Rate coefficients have lower case "k".

We have changed the equilibrium constant on line 108 and Equation (4) as K_{eq}, and the rate coefficient as lowercase k in SI Table S. 1 and S. 3.

3.9 L/3 H_0 is estimated (Thornton et al, 2008) to be 3900 M atm-1. Why is this cited in different units to the effective solubility (Hˆcc). How good is this "estimate" and on what data is it based (I believe Hanson 1992, who also lists a T-dependence)?

450   We have changed the units of the effective solubility as M atm^{-1} in the new MS. There is no particular reason other than an oversight in writing the manuscript that the temperature dependence was not taken into account. Thank you for pointing it out. H_0 is the physical Henry's law constant, the original data used in this manuscript is from Golden et al. (1990) and Hanson et al. (1992). We agree it is better to use H_0 with the temperature dependent formula recommended by IUPAC as follows:

$$H_0 = 9.5 \times 10^{-6} \exp\left(\frac{5910}{T}\right) M\ atm^{-1}$$

455   At 298K, H_0 equals to 3897.13 M atm^{-1} calculated from the formula, and the estimation as 3900 M atm^{-1} may cause small deviation.

We changed the equation 4 in the revised MS as:

$$H^{cc} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right) \times A_{HO_2} = 9.5 \times 10^{-6} exp\left(\frac{5910}{T}\right) \times \left(1 + \frac{K_{eq}}{[H^+]}\right) \times A_{HO_2} \tag{4}$$

In our model, the T-dependence formula is used in the MARK model now. No difference between the original and revised

460   results have been shown because at 298K, with the T dependent parametrization a value of 3897.13 M atm^{-1} is obtained for H_0 while a value of 3900 was used before.

3.10 L101 Define [xi]_equ. In the line above only [xi] is mentioned.

In the bulk condensed phase of aerosol particle, the effective concentration $[x_i]_{equ}$, rather than total concentration of ions,

465   should be calculated because of the high ionic strength. We added "effective" to the original sentence under the equation (9) in the revised MS and show the equation of effective $[Cu^{2+}]_{equ}$ in the aerosol particle condensed phase as Equation (11).

5.1 L105 "steady-state" HO$_2$ concentration. Why "steady-state"?

As discussed below (please see response to Comment 1.5), the parameterization proposed by IUPAC is originally from the

470   heterogeneous modeling with liquid droplets and modified by the Resistance Model (Danckwerts, 1951;Schwartz, 1984;Schwartz, 1986;Ammann et al., 2013;Davidovits et al., 2006). The Resistance Model is based on the assumption of steady-state solutions (liquid water cloud droplets). The novel parameterization proposed by Song et al. is still built on the basic framework of the Resistance model, thus only steady-state HO$_2$ concentration can be calculated and in consequence this novel parameterization has the limitation of steady-state assumption.

475   In the revised MS on line 361 we added statement of the limitation of the novel empirical equation.

3.11 L110 k_eff is listed in the equation 11. This appears to be defined 57 lines later, but not always in the same manner.

We defined k_{eff} as "the comprehensive reaction rate coefficient encompasses both HO$_2$ dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO$_2$ uptake process." on line 147 just under the Equation (13) in Section 2.2.3

480   of the revised MS. This is the place where the definition first appeared. We deleted the conflict definitions below.

3.12 Tab1 (and abstract) the accommodation coefficient is not defined, as far as I can see.

We have added the definitions of relevant parameters of the parameterization in the revised MS Abstract. Please see response to comment 3.4.

5.2 Tab1 The data of Lakey 2015/2016 and Zou 2019 are not mentioned (Moon = Lakey ???)

Following consultation with the Leeds group, we added the published data by Lakey et al. 2016 and Zou et al. 2019 in the revised MS Table 1.

The study of Lakey et al, 2015 measured γ_{HO_2} on single component organic aerosols and the Cu ion concentration was not high enough (~0.7-1.3$\times10^{-6}$ to 5.5$\times10^{-4}$ M) to measure α. Thus, we did not include the data from Lakey (2015) in the Table 1. The citations used in the original MS are corrected based on the Short Comment to this paper from Prof. D. Heard and the response to that. Please see the response to the first short comment.

Table 1: γ_{HO_2} under lab conditions for Cu^{2+}-doped inorganic aerosols.

Aerosol type	RH/%	Estimation of [Cu] in aerosol/M	α_{HO_2}	Ref.
NH_4HSO_4	75%	0.0059−0.067*	0.40±0.21	(Mozurkewich et al., 1987)
$(NH_4)_2SO_4$	45%	0.5	0.53±0.13	(Taketani et al., 2008)
$(NH_4)_2SO_4$	42%	0.16	0.5±0.1	(Thornton and Abbatt, 2005)
$(NH_4)_2SO_4$	53−65%	0.5−0.7*	0.4±0.3	(George et al., 2013)
$(NH_4)_2SO_4$	65%	0.57	0.26±0.02	(Lakey et al., 2016)
$(NH_4)_2SO_4$	51%	0.0027	0.096±0.024	(Zou et al., 2019)
$(NH_4)_2SO_4$	43%	0.38	0.355±0.023	This work
NaCl	53%	~0.5	0.65±0.17	(Taketani et al., 2008)
KCl	75%	5% of KCl solution	0.55±0.19	(Taketani et al., 2009)
$LiNO_3$	75%	0.03−0.0063*	0.94±0.5	(Mozurkewich et al., 1987)

*Cu concentration is in molality (mol kg^{-1}).

3.13 Tab2 Add units, do not capitalize K…

Table 2 is moved to the Supplemental Information of the revised MS as Table S.1. In Table S.1 we add the units of reaction rate constants as: "k_{298}/M^{-n} s^{-1}" in the header.

6.1 …and move to supplementary information

18

This is a good suggestion. Please see the response to Comment 3.1. We moved this part and Table 3, Table 4 and Table 5 to the SI as Table S. 1, S. 2, S. 3 and S. 4.

505   3.14 Tab3 K should be capitalized (eqm.)

We changed to a capital K_{298}.

3.15 L146 annual average contribution. Does this refer to a global average?

It does not refer to a global average. It is the annual average contribution across China based on the research of Tao et al., (Tao
510   et al., 2017). We added "across China" in the original statement on line 173 as: "…contribution of inorganic aerosol to $PM_{2.5}$ is between 25% and 48% across China (Tao et al., 2017)…"

5.3 Fig1 Please explain why the uptake coefficient continues to increase at pH > 5 whereas k_eff decreases.

We agree that it was not clearly explained why this is the case. A higher pH will increase the solubility of HO_2. Moreover,
515   since the rate of O_2^- with Cu^{2+} is larger than the rate of HO_2, with larger pH, O_2^- will be more dominant over HO_2 thus increase the reaction rate. γ_{HO_2} therefore is higher in alkaline environments. However, the optimization simulation of k_{eff} try to avoid the influence of pH in the range of 3-6. pH influence on γ_{HO_2} is embodied in H_{corr} $\left(= H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right)\right)$. With the fixed value of α_{HO_2} and sharply increasing H_{corr} with pH, the combined reaction rate k_{eff} peaks in the 4-5 pH range, and then quickly declines calculated by Equation (15).

520

In the revised MS, we deleted the original k_{eff} graph (Figure 1) to avoid confusion in the understanding of the entire reaction system, and we have included the quasi-first order reaction rate constant k_{het} of the gas phase HO_2 as in the new Figure 1. Figure 1 and the explanation are corrected as follows in the revised MS:
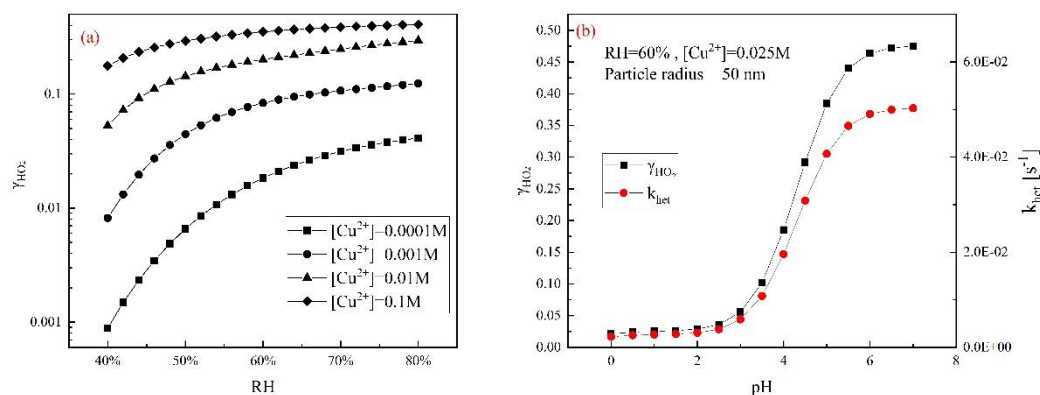
525 Figure 1: Influence of various parameters upon γ_{HO_2} predicted by the MARK model. (a) γ_{HO_2} increases with the *RH* at different [Cu^{2+}]; (b) γ_{HO_2} denoted by black squares and black line and k_{het} in red circles and red line increase with aerosol particle condensed phase pH.

We also changed the analysis in the revised MS in Section 3.1 last paragraph as follows:

530 "γ_{HO_2} presents a sigmoid-shaped growth with aerosol particle condensed phase pH. In the model, it is found that as the pH rises, the uptake coefficient rises rapidly because HO_2 is a weak acid (pKa = 4.7) and has a low solubility in an acidic environment. The higher condensed phase pH is favorable for the dissolution equilibrium of the gas phase HO_2.. This trend is consistent with the observed second-order rate constant of HO_2/O_2^- reviewed by Bielski et al. 1985 (Bielski et al., 1985). Moreover, aqueous phase reaction rates of HO_2/O_2^- and Cu^{2+}/Cu^+ increase with the increasing of condensed phase pH because
535 in alkaline environment HO_2 is more likely becoming O_2^- which has quicker reaction rate with Cu^{2+}/Cu^+. The pH of the ambient atmospheric aerosol is measured generally below 5 even when the concentration of NH_3 is high as in Beijing and Xi'an (Ding et al., 2019;Guo et al., 2017) with a range of 3-5. At this range, γ_{HO_2} is highly affected by aerosol condensed phase pH may mainly because of the change of solubility."

540 3.16 L166 k_eff is defined as a comprehensive reaction rate constant. . .. . .during heterogeneous uptake. On L210, K_eff is defined as the rate of HO2 aqueous reaction with copper ions.

Please see response to Comment 3.11 above.

1.2 L175 The parameterisations listed do not include that of IUPAC, which includes more recent laboratory data than those
545 listed.

Please see the response to Comment 1.1.

1.3 L180 Based on the data of Lakey et al, IUPAC list a rate coefficient for HO2 (O2-) with Cu ions of 5x10^5. This is orders of magnitude lower that those listed.

550

We added the following explanation in Section 3.2 the last paragraph of the revised MS on line 245:

"There is more discussion about this reaction rate. IUPAC (Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.) proposed the effective rate coefficient for the reaction of HO_2 (O_2^-) with Cu ions as 5×10^5 M^{-1} s^{-1} to achieve the best fit based on the calculation results from Lakey et al. (2016). This
555 assumption is not in accordance with the aqueous reaction rate coefficient from other databases mentioned below, and needs further laboratory measurements to confirm it. According to the aqueous reaction rate coefficient from NIST and the latest measurement result (Lundström et al., 2004;Huie, 2003), the rate coefficient of HO_2 with Cu^{2+} is 1×10^8 or 1.2×10^9 M^{-1} s^{-1} at

pH= 2 and pH=1, respectively. These two rate coefficients were quantified in a low pH environment (pH=2 for 1.2×10^9 M^{-1} s^{-1} and pH=1 for 1×10^8 M^{-1} s^{-1}). At the same time, the reaction rate of O_2^- with Cu^{2+} is 8×10^9 M^{-1} s^{-1} for pH in the range 3-6.5

560 (Huie, 2003). At higher pH, the reaction rate of HO_2 with Cu^{2+} may change, but it is unknown whether it will decrease by four orders of magnitude. Further kinetics experiments are needed at varying pH to verify the reaction rate coefficient of Cu^{2+} ions with HO_2 and O_2^- in aqueous solution."

4.2 Fig2 Why are the data of Lakey not listed (or are these Moon ??)

565 Please see the response to Comment 4.1, and the response to the Short Comment by D. Heard.

5.4 Fig2 Taketani also have uptake coefficients in the absence of Cu that are just as high as the single point at about 0.5 M. Why are the other datapoints of Taketani selectively omitted here?

The focus of this manuscript is to investigate the influence of copper ions on HO_2 heterogeneous reactions and it proposes a

570 new empirical parameterisation applicable to ambient copper ion containing aerosols. Therefore, we only included the experimental results of Taketani et al. obtained with copper-doped inorganic aerosols and did not include other experimental studies of inorganic aerosol not doped with copper ions, which are inconsistent with other measurements, perhaps owing to differences in experimental conditions in the laboratory (George et al., 2013) as follows. The mechanism of HO_2 uptake with single component aerosols (such as $(NH_4)_2SO_4$) is still not fully understood. Moreover, HO_2 uptake coefficient measurement

575 is highly affected by experimental conditions such as HO_2 concentration, reaction time, etc. Some data from Taketani et al. are not consistent with other measurements within the community. Taketani reported γ_{HO_2} = 0.11±0.03 at 45% RH, 0.15±0.03 at 55% RH, 0.17±0.04 at 65% RH and 0.19±0.04 at 75% RH when the HO_2 initial concentration was 1×10^8 molecule cm^{-3}, which are inconsistent with results from Thornton and Abbatt. Thornton and Abbatt concluded that the γ for wet particles of $(NH_4)_2SO_4$ is < 0.01 at ~42% RH and a HO_2 ambient concentration of ~1×10^8 molecule cm^{-3} from extrapolation based on their

580 research with HO_2 initial concentration at 5×10^{10} molecule cm^{-3}. George et al. (2013) reported γ_{HO_2} as 0.003±0.005 at 55% RH and 0.01±0.01 at 65-75% RH at HO_2 initial concentration of 1.5×10^8 -1.5×10^9, also much lower than the measurements of Taketani et al. The initial HO_2 concentration and Cu^{2+} contamination will also affect γ_{HO_2}.

1.4 L188 what is the "current parameterised equation". From whom is it?

585 Please see the response to Comment 1.1.

1.5 L201 This text ignores the fact that the IUPAC parameterisation accurately reproduces the lab studies from Lakey et al. Is the empirical parameterisation that Song et al propose really superior to the IUPAC one, which has a physical basis?

Please see the response to Comment 1.3 above. We agree with the referee, that the IUPAC parameterization reproduces the

590 laboratory studies from Lakey et al. with k_{TMI} (defined as the second order rate coefficient for the reaction of HO_2 /O_2^- with

21

transition metal ions) equal to 5×10^5 M^{-1} s^{-1}. However, we also note that IUPAC states "the parameterization suggested here is very sensitive to the solubility of HO$_2$ (H_{HO2}), its temperature dependence and on the aerosol pH", which we attempt to address in our new parameterisation.

The parameterization proposed by IUPAC is originally from the heterogeneous modeling with liquid droplets which was
595 modified to become the Resistance Model (Danckwerts, 1951;Schwartz, 1984;Schwartz, 1986;Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.;Davidovits et al., 2006). The Danckwerts expressions with analytical solutions include the effect of Henry's law solubility on gas uptake, liquid-phase reactions of the solvated molecules, and the mass accommodation coefficient exist for a few limited conditions. In general, the coupled differential equations must be solved numerically. After Danckwerts, Schwartz et al. proposed a parameterization
600 which came to be known as "the Resistance Model". The Resistance Model has been shown to provide a good approximation (within a few percent) to the numerical solution of the coupled differential equations. The whole framework of this parameterized equation was based on the assumption of steady-state solutions (liquid water cloud droplets) and decouple the differential equations for each heterogeneous process while does not take into account the physical and chemical characteristics of the ambient aerosol. The empirical equation proposed by Song et al. has made related improvements including the "*salting*
605 *out*" effects of gas molecular and effective copper ion concentration. Although still with limitations, the novel empirical equation can be applied to the estimation of γ_{HO_2} with aerosol particles.

3.17 L213 where does this expression for the uptake coefficient come from?

The definition of γ_{HO_2} is from the Appendix A of Hanson et al., 1994 (Hanson et al., 1994). We add the citation on line 270 in
610 Section 3.3 second paragraph as: "Hanson et al. (1994) proposed the definition of the uptake coefficient as $\gamma = \alpha(1 - \frac{c_{a,surf}}{H^{cc}c_{g,surf}})$ where $c_{a,surf}$ is the suface concentration of the reactant, $c_{g,surf}$ is the gas phase concentration. In the process of HO$_2$ uptake, we deduce the parameterized equation of γ_{HO_2} in the framework of the resistance model."

6.2 L265 section 3.4.2. could be move to SI
615 This is a good suggestion. Please see the response to Comment 3.1.

We move section 3.4.2. to the SI.

5.5 L312 The work of Lakey et al is cited. Where are their data?

Please see the response to Comment 5.2 and the response to the Short Comment by D. Heard.
620

2.2 How much "lower" can the uptake coefficient be in the presence of organics?

Please see the response to Comment 2.1.

625   This is a good suggestion. Please see the response to Comment 3.1.

   We move section 3.4.5 to the SI.

References:

630   Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI - heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, 10.5194/acp-13-8045-2013, 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.

Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Pöschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy, semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, Physical Chemistry Chemical
635   Physics, 18, 12662-12674, 2016.

Bielski, B. H., Cabelli, D. E., Arudi, R. L., and Ross, A. B.: Reactivity of HO_2/O_2^- radicals in aqueous solution., Journal of physical and chemical reference data, 14, 1041-1100, 1985.

Chameides, W. L., and Stelson, A. W.: Aqueous-phase chemical processes in deliquescent seasalt aerosols, Ber Bunsen Phys Chem, 96, 461-470, 1992.

640   Danckwerts, P.: Absorption by simultaneous diffusion and chemical reaction into particles of various shapes and into falling drops, Transactions of the faraday society, 47, 1014-1023, 1951.

Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T., and Worsnop, D. R.: Mass accommodation and chemical reactions at gas-liquid interfaces, Chemical Reviews, 106, 1323-1354, 10.1021/cr040366k, 2006.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939-
645   7954, 10.5194/acp-19-7939-2019, 2019.

Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, Environ. Sci. Technol., 51, 2611-2620, 10.1021/acs.est.6b06151, 2017.

George, I. J., Matthews, P. S. J., Whalley, L. K., Brooks, B., Goddard, A., Baeza-Romero, M. T., and Heard, D. E.: Measurements of uptake coefficients for heterogeneous loss of HO2 onto submicron inorganic salt aerosols, Physical Chemistry Chemical Physics, 15, 12829-12845,
650   2013.

Golden, D. M., Bierbaum, V. M., and Howard, C. J.: Re-evaluation of the bond-dissociation energies (Delta-Hdbe) for H-OH, H-OOH, H-OO-, H-O., H-OO-, and H-OO, J Phys Chem-Us, 94, 5413-5415, 10.1021/j100376a046, 1990.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci Rep-Uk, 7, 12109, 10.1038/s41598-017-11704-0, 2017.

655   Hanson, D. R., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of OH and HO2 radical uptake coefficients on water and sulfuric-acid surfaces, J Phys Chem-Us, 96, 4979-4985, Doi 10.1021/J100191a046, 1992.

Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric-acid aerosol: A framework for model calculations, J. Geophys. Res.-Atmos., 99, 3615-3629, 10.1029/93jd02932, 1994.

Hsu, S. C., Liu, S. C., Lin, C. Y., Hsu, R. T., Huang, Y. T., and Chen, Y. W.: Metal compositions of PM10 and PM2.5 aerosols in Taipei
660   during spring, 2002, Terrestrial Atmospheric and Oceanic Sciences, 15, 925-948, 10.3319/tao.2004.15.5.925(adse), 2004.

Hsu, S. C., Liu, S. C., Tsai, F., Engling, G., Lin, II, Chou, C. K. C., Kao, S. J., Lung, S. C. C., Chan, C. Y., Lin, S. C., Huang, J. C., Chi, K. H., Chen, W. N., Lin, F. J., Huang, C. H., Kuo, C. L., Wu, T. C., and Huang, Y. T.: High wintertime particulate matter pollution over an offshore island (Kinmen) off southeastern China: An overview, J. Geophys. Res.-Atmos., 115, 10.1029/2009jd013641, 2010.

Huie, R. E.: NDRL/NIST Solution Kinetics Database on the WEB, Journal of Research (NIST JRES)-, 108, 2003.

665   Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131-2159, 10.1016/s1352-2310(99)00462-8, 2000.

Kolb, C., Worsnop, D., Zahniser, M., Davidovits, P., Keyser, L., Leu, M.-T., Molina, M., Hanson, D., Ravishankara, A., and Williams, L.: Laboratory studies of atmospheric heterogeneous chemistry, in: Progress and problems in atmospheric chemistry, World Scientific, 771-875, 1995.

Kuang, Y., Tao, J., Xu, W., Yu, Y., Zhao, G., Shen, C., Bian, Y., and Zhao, C.: Calculating ambient aerosol surface area concentrations
670   using aerosol light scattering enhancement measurements, Atmos. Environ., 216, 116919, https://doi.org/10.1016/j.atmosenv.2019.116919, 2019.

Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO2 Uptake Coefficients onto Single Component Organic Aerosols, Environ. Sci. Technol., 49, 4878-4885, 10.1021/acs.est.5b00948, 2015.

Lakey, P. S. J., George, I. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Organics Substantially Reduce HO2 Uptake onto
675   Aerosols Containing Transition Metal ions, Journal of Physical Chemistry A, 120, 1421-1430, 10.1021/acs.jpca.5b06316, 2016.

Lelieveld, J., and Crutzen, P. J.: The role of clouds in tropospheric photochemistry, J Atmos Chem, 12, 229-267, 10.1007/bf00048075, 1991.

Lundström, T., Christensen, H., and Sehested, K.: Reactions of the HO2 radical with OH, H, Fe2+ and Cu2+ at elevated temperatures, Radiation Physics and Chemistry, 69, 211-216, 2004.

680 Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, Atmos. Chem. Phys., 13, 509-519, 10.5194/acp-13-509-2013, 2013.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Poschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491-9522, 2009.

685 Mozurkewich, M., Mcmurry, P. H., Gupta, A., and Calvert, J. G.: Mass Accommodation Coefficient for Ho2 Radicals on Aqueous Particles, Journal of Geophysical Research-Atmospheres, 92, 4163-4170, 1987.

Price, H. C., Mattsson, J., Zhang, Y., Bertram, A. K., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., and Rickards, A. M.: Water diffusion in atmospherically relevant α-pinene secondary organic material, Chem Sci, 6, 4876-4883, 2015.

Sander, R.: Modeling atmospheric chemistry: Interactions between gas-phase species and liquid cloud/aerosol particles, Surveys in Geophysics, 20, 1-31, 1999.

690 Schwartz, S. E.: Gas phase and aqueous phase chemistry of HO_2 in liquid water clouds, J. Geophys. Res.-Atmos., 89, 1589-1598, 10.1029/JD089iD07p11589, 1984.

Schwartz, S. E.: Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, in: Chemistry of multiphase atmospheric systems, Springer, 415-471, 1986.

Shiraiwa, M., Pfrang, C., and Poschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of
695 interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, Atmos. Chem. Phys., 10, 3673-3691, 10.5194/acp-10-3673-2010, 2010.

Song, S. J., Gao, M., Xu, W. Q., Shao, J. Y., Shi, G. L., Wang, S. X., Wang, Y. X., Sun, Y. L., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

700 Taketani, F., Kanaya, Y., and Akimoto, H.: Kinetics of heterogeneous reactions of HO_2 radical at ambient concentration levels with $(NH_4)_2SO_4$ and NaCl aerosol particles, The Journal of Physical Chemistry A, 112, 2370-2377, 2008.

Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous loss of HO_2 by KCl, synthetic sea salt, and natural seawater aerosol particles, Atmos. Environ., 43, 1660-1665, 2009.

Tan, Z., Hofzumahaus, A., Lu, K., Brown, S. S., Holland, F., Huey, L. G., Kiendler-Scharr, A., Li, X., Liu, X., and Ma, N.: No Evidence for
705 a Significant Impact of Heterogeneous Chemistry on Radical Concentrations in the North China Plain in Summer 2014, Environ. Sci. Technol., 2020.

Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning $PM_{2.5}$ chemical composition, aerosol optical properties and their relationships across China, Atmos. Chem. Phys., 17, 9485, 2017.

Thornton, J., and Abbatt, J. P. D.: Measurements of HO_2 uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss,
710 J. Geophys. Res.-Atmos., 110, 10.1029/2004jd005402, 2005.

Thornton, J. A., Jaegle, L., and McNeill, V. F.: Assessing known pathways for HO_2 loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, Journal of Geophysical Research: Atmospheres, 113, 2008.

Zhou, J., Murano, K., Kohno, N., Sakamoto, Y., and Kajii, Y.: Real-time quantification of the total HO_2 reactivity of ambient air and HO_2 uptake kinetics onto ambient aerosols in Kyoto (Japan), Atmos. Environ., 223, 117189, https://doi.org/10.1016/j.atmosenv.2019.117189,
715 2020.

Zou, Q., Song, H., Tang, M., and Lu, K.: Measurements of HO_2 uptake coefficient on aqueous $(NH_4)_2SO_4$ aerosol using aerosol flow tube with LIF system, Chinese Chemical Letters, https://doi.org/10.1016/j.cclet.2019.07.041, 2019.

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Influence of aerosol copper on HO₂ uptake: A novel parameterized equation

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Abstract. ~~The heterogeneous~~Heterogeneous uptake of ~~hydroxyl peroxy~~hydroperoxyl radicals (HO₂) ~~on aerosol~~onto aerosols has been proposed to be a significant sink of HOx~~, thus could influence~~ and hence the atmospheric oxidation capacity. Accurate calculation of the HO₂ uptake coefficient γ_{HO_2} is ~~the~~ key to quantifying ~~its~~ the potential impact of this atmospheric ~~effects~~process. Laboratory studies show that γ_{HO_2} ~~varies~~can vary by orders of magnitude due to ~~change~~changes in aerosol properties, especially ~~those of~~ aerosol soluble copper (Cu) and aerosol liquid water content (ALWC). In this study~~,~~ we ~~develop~~present a state-of-the-art model to simulate both gas and aerosol phase chemistry~~. A novel parameterized equation~~ for the uptake of HO₂ ~~considering change in RH and aerosol~~onto Cu~~is~~ -doped aerosols. Moreover, a novel parameterization of HO₂ uptake was developed that considers changes in relative humidity (*RH*) and condensed phase Cu ion concentrations and which is based on a model optimization ~~toward all available lab experiments.~~ using previously published laboratory and new laboratory data included in this work. The new parameterization is as follows:

$$\frac{1}{\gamma_{HO_2}} = \frac{1}{\alpha_{HO_2}} + \frac{3 \times \upsilon_{HO_2}}{4 \times 10^6 \times R_d H_{corr} RT \times (5.87 + 3.2 \times \ln(ALWC/[PM] + 0.067)) \times [PM]^{-0.2} \times [Cu^{2+}]^{0.65}}$$

where α_{HO_2} is the mass accommodation coefficient of HO₂ which is the probability that a HO₂ molecule colliding with the aerosol surface leads to dissolution, reaction or volatilization, υ_{HO_2} is the mean molecular speed of HO₂ [cm s⁻¹]. ~~$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{3 \times \upsilon}{4 \times 10^6 \times R_d H_{corr} RT \times (5.87 + 3.2 \times \ln(ALWC/[PM] + 0.067)) \times [PM]^{-0.2} \times [Cu^{2+}]^{0.65}}$~~

R_d is the Count Median Radius of the aerosols [cm], H_{corr} is the Henry's constant [mol cm⁻³ atm⁻¹] corrected for solution pH ($H_{corr} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right)$, where H_0 is the physical Henry's law constant), R is the gas constant [cm³ atm K⁻¹ mol⁻¹], T is the temperature [K] and [PM] is the mass concentration of particles [μg m⁻³]. According to the new equation, highly variable HO₂

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uptake coefficients (median value ~0.1) were ~~diagnosed~~obtained for the North China Plain and the impact of HO$_2$ uptake on the ROx (=OH + HO$_2$ + RO$_2$) budget ~~is~~was assessed.

1 Introduction

The atmospheric cleansing capacity of the troposphere is largely determined by the concentrations of the hydroxyl radical, which are closely linked with the concentrations of the ~~hydroxyl peroxy~~hydroperoxyl (HO$_2$) radical. In the established chemical mechanism, the coupling of OH and HO$_2$ is strongly determined by the reaction of OH + VOCs~~/~~ (volatile organic compounds)/CO/HCHO/CH$_4$/H$_2$/SO$_2$ and HO$_2$ + NO (Seinfeld, 1986). The reactivity from aerosol uptake cannot compete with the known gas phase reactivity of OH, whereas it may compete with the reactivity of NO toward HO$_2$ under some conditions such as low NO (Tang et al., 2017). For high aerosol mass load, the reaction rate of HO$_2$ with aerosol particles could be fast enough to influence the concentration of HOx radicals, and consequently, reduce ozone production from HO$_2$+NO (Kanaya et al., 2009;Li et al., 2019b).

From a global perspective, the impact of HO$_2$ uptake on the calculated HOx concentrations is diagnosed to be about 10~40 ~~%~~% (Jacob, 2000;Whalley et al., 2015;Whalley et al., 2010;Mao et al., 2010;Li et al., 2019b;Li et al., 2019a) ~~when~~and often the value of γ_{HO2} (the heterogeneous uptake coefficient~~(Schwartz and Meyer, 1986)~~ (Schwartz, 1984;Schwartz, 1986)) is assumed to be a single value, 0.2 (Tie et al., 2001;Martin et al., 2003). The ~~diagnosed~~ impact of HO$_2$ uptake is lowered when ~~using~~a parameterized equation of γ_{HO_2} is used without considering the influence of transition metal ions (TMIs~~)(Thornton et al., 2008))~~ (Thornton et al., 2008), ~~and~~however, still, a significant impact on the calculated [OH] and O$_3$ production rate ~~aresuggested~~are suggested for air masses over Chinese megacity areas~~(Macintyre and Evans, 2011)~~ (Macintyre and Evans, 2011). A model study (Xue et al., 2014) considering the aerosol uptake of HO$_2$ showed an impact on the simulated HO$_2$ concentrations and local O$_3$ production rates in Chinese urban regions: Beijing, Shanghai, and Guangzhou. Furthermore, researchers have ~~pointed out~~proposed that in the North China Plain (Li et al., 2019a;Li et al., 2019b), the reduced ~~of~~HO$_2$ uptake ~~on~~owing to reduction of aerosol ~~is a~~surface area is considered to be the key reason for the ~~increase in~~increased surface ozone concentration over the last few years ~~due to the suppression of NOx lifetime with~~ when a value of 0.2 was used for γ_{HO_2} ~~fixed at 0.2.~~.

Previous studies show that the value of γ_{HO_2} from the laboratory, field, and modeling studies ~~span~~spans several orders of magnitude, ranging from <0.002 for dry aerosols (Cooper and Abbatt, 1996;Taketani et al., ~~2008a~~2008;George et al., 2013) to 0.2 for ~~neutralized~~liquid deliquesced aerosols~~(Thornton and Abbatt, 2005).~~. Much higher values of γ_{HO_2} have been measured and calculated for Cu-doped aerosols (Mozurkewich et al., 1987;Taketani et al., ~~2008b;Thornton and Abbatt,~~ ~~2005;~~2008;Thornton et al., 2008;Cooper and Abbatt, 1996;Lakey et al., 2016b;George et al., 2013). For fine particles, the reactions of HO$_2$ with soluble Cu ions may be fast enough ~~to be~~thus the uptake coefficient is limited by the mass accommodation coefficient α. Due to the widespread distribution of Cu^{2+} ion in ambient particles, the absence of an accurate

evaluation of γ_{HO_2} is one of the largest uncertainties for the determination of the impact of HO₂ uptake on ~~worrisome and~~ pressing atmospheric issues such as ozone formation.

790   In this study, we reanalyzed ~~various results on~~several datasets of the aerosol uptake of HO₂ from ~~both~~ laboratory ~~and field~~ studies reported in the literature ~~and propose~~, a new dataset for HO₂ uptake coefficient onto Cu-dopped ammonium sulphate aerosols at 43% relative humidity and proposed a novel parameterized equation for the prediction of γ_{HO_2} that best fits all the ~~lab~~laboratory results. Furthermore, for a field campaign, we also calculated γ_{HO_2} according to the novel parameterized equation and the impact of HO₂ uptake on HOx (=OH + HO₂) budget ~~were~~was evaluated.

795 **2 Materials and Methods**

2.1 The Model

A Multiphase Reaction Kinetic Model (MARK) is developed in this study for the simulation of γ_{HO_2} for ~~both the lab and field experiments.~~the laboratory experiments. The reaction mechanism and reaction rate constants are summarized in Table S.1 – S.4in the Supplementary Information (SI). The MARK model is currently capable of simulating inorganic deliquescent

800 aerosol at ambient pressure and temperature. The model directly calculates the ~~net~~quasi-first order gas phase uptake loss rate, ~~k$_{net}$,~~k_{het} (s^{-1}), in Eq. (1). In this model, aerosol liquid water content (~~L)[~~ALWC) [g cm^{-3}] is more pertinent than surface density because of the influence of the *RH* on the uptake process (Kuang et al., 2018;Bian et al., 2014).

$$\frac{d[HO_2]}{dt} = -k_{het} \times [HO_2] \tag{1}$$

$$k_{het} = (\frac{r_p}{D_g} + \frac{4}{\gamma \bar{v}})^{-1} \times \frac{3L}{r_p} = (\frac{R_d}{D_g} + \frac{4}{\gamma v_{HO_2}})^{-1} \times \frac{3ALWC}{\rho R_d} \tag{2}$$

805 ~~where r_p is the aerosol particle radius[cm], $\bar{v}$~~where R_d is Count Median Radius of aerosols[cm] , v_{HO_2} is the mean molecular speed of HO₂ [cm s^{-1}] and D_g is the gas phase diffusion coefficient [cm²s^{-1}], ρ is the density of the aerosol particles [g cm^{-3}]. The units of aqueous reagents are converted to [molecule cm^{-3}] in the model by k_{mt}.

An approach to combine both gas phase molecular diffusion and liquid phase interface mass transport processes is through one variable called k_{mt} (Schwartz, 1984;Schwartz, 1986), which is used in the calculation for gas-liquid multiphase

810 reactions in many modelling studies (Lelieveld and Crutzen, 1991;Chameides and Stelson, 1992;Sander, 1999;Hanson et al., 1994). The definition of k_{mt} is:

$$k_{mt} = (\frac{R_d^2}{3D_g} + \frac{4R_d}{3v_{HO_2}\alpha})^{-1} \tag{3}$$

k_{mt} is used to connect the gas phase reactions and the aerosol condensed phase reactions. The rate of gas phase reactants (X) diffusing and dissolving to the condensed phase can be calculated in the framework of aqueous phase reactions as

815 $k_{mt\_X} \times ALWC$ (where X is the reactant molecule). Moreover, the conversion rate of aqueous phase reactants to gas phase can be calculated as $\frac{k_{mt\_X}}{H^{cc} \times RT}$ where H^{cc} is the effective Henry's law constant [M atm^{-1}]. The unit of k_{mt} is s^{-1}, as k_{mt} contains

the conversion from m_{air}^{-3} of the gas phase molecule concentrations to m_{aq}^{-3} of the aqueous phase molecule concentrations and in the other direction. For larger particles (radius >1 μm), k_{mt} is mainly determined by gas phase diffusion of HO_2. For smaller particles (radius <1 μm) k_{mt} is mainly determined by the accommodation coefficient (α). The MARK model can simultaneously simulate gas and liquid two-phase reaction systems in the same framework.

The aerosol particle condensed phase is not an ideal solution in which an effective Henry's law constant H^{cc} should be applied in the model calculation, considering the effects of solution pH and the small gas phase molecule (such as HO_2, OH, O_2 ect.) "*salting out*" effect due to the existance of electrolytes in the solution (Ross and Noone, 1991). This study uses the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007) to calculate the ALWC and components concentrations for metastable deliquescent aerosols. The effective Cu^{2+} concentration in the aqueous phase, which is strongly influenced by non-ideal solution ionic strength, is also calculated following Ross and Noone (Ross and Noone, 1991).

~~is the mean molecular speed of HO_2 [cm s⁻¹]. and D_g is the gas phase diffusion coefficient [cm²s⁻¹]. The units of aqueous reagents are converted to molecules cm⁻³. Aerosol particle bulk phase is not an ideal solution in which an effective Henry's law constant H^{cc} should be applied in the model calculation, considering the effects of solution pH and the "*salting out*" effect of HO_2 and other gas reactants(Ross and Noone, 1991). This study uses the ISORROPIA II thermodynamic model(Fountoukis and Nenes, 2007) to calculate the properties of metastable deliquescent aerosols. The effective Cu^{2+} concentration in the aqueous phase, which is strongly influenced by non-ideal solution ionic strength, is also calculated following Ross and Noone(Ross and Noone, 1991).~~

2.2 Corrections ~~on~~to γ_{HO_2} in ~~MARKM~~the MARK model

2.2.1 Henry's law of gas phase reactants

~~Aerosol bulk~~The aerosol particle condensed phase solution is not an ideal solution~~,~~ as commented before. The addition of an electrolyte to water interferes with the gas dissolution and the organization of water molecules around the gas. This frequently results in a decrease in the solubility, or a "*salting out*" effect. This *salting out* effect is frequently a linear function of the molar ionic strength *I*. H^{cc} is the effective Henry's law constant ~~of HO_2 [mol cm⁻³~~[M atm⁻¹], H_0 is the physical Henry's law constant, estimated to be about 3900 M atm⁻¹ at 298K~~(Thornton et al., 2008)~~. k_{eq} for HO_2 (Thornton et al., 2008;Golden et al., 1990;Hanson et al., 1992) and its temperature dependence is given accordingly to the IUPAC recommendation (Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.). H_0 should be corrected by the solution pH and the "salting out" effect. In the MARK model, these two corrections are incorporated as H^{cc}:

$$H^{cc} = H_0 \times \left(1 + \frac{K_{eq}}{[H+]}\right) \times A_{HO_2} = 9.5 \times 10^{-6} \, exp\left(\frac{5910}{T}\right) \times \left(1 + \frac{K_{eq}}{[H+]}\right) \times A_{HO_2} \quad (4)$$

K_{eq} is the solution equilibrium constant for HO_2 in the gas phase. ~~Activity~~ . The activity coefficient *A* for HO_2 and other neutral small ~~molecule~~molecules can be expressed as~~(Ross and Noone, 1991)~~ (Ross and Noone, 1991):

~~$$H^{cc} = H_0 \times (1 + \frac{k_{eq}}{[H+]}) \times A_{HO_2} \quad (3)$$~~

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$$A_{HO_2} = 10^{-0.1 \times I} \tag{45}$$

~~In MARK model, the effective Henry's constants of main gas phase reactant are corrected based on above equations.~~ ~~H^{cc}~~According to this correction, H^{cc} of HO$_2$ increases with *RH* and decreases quickly after [Cu^{2++}] reaches 0.1M in aerosol liquid phase, which limits γ_{HO_2} ~~on~~at high ~~Cu~~Cu^{2+} concentration.

~~2.~~2.2.2 Aerosol ~~bulk~~particle condensed phase ~~Cu~~Cu^{2+} molality calculation

Inorganic species in ambient aerosol particles may be in the form of aqueous ions, or in the form of precipitated solids in thermodynamic equilibrium with atmospheric gases and water vapor. The salts in the metastable aerosol are all dissolved in the aqueous phase. For meta-stable aerosols, this paper uses thermodynamic models to calculate ~~aerosol properties.~~ALWC and aerosol particle condensed phase component concentrations. In this work ISORROPIA II~~(Fountoukis and Nenes, 2007;Capps et al., 2012) is a~~ (Fountoukis and Nenes, 2007;Capps et al., 2012) thermodynamic equilibrium model for inorganic aerosol ~~system~~systems is used to take into account this.

In ambient aerosol, though the Fe concentration is about 10−100 times (Mao et al., 2013a) higher than that of Cu, for an aerosol pH ranging from 3−6, the solubility of Fe (primarily Fe^{2+}) is rather small (Fang et al., 2017;Hsu et al., 2010a;Baker and Jickells, 2006;Oakes et al., 2012). The reaction rates of Fe/Mn for liquid phase HO$_2$ in aerosol is about 100 times slower than it is for Cu. For these reasons, the influence of aerosol Fe and Mn on HO$_2$ uptake can be neglected compared to Cu or scaled as equivalent [Cu^{2+}]. Thus, in this paper, we only focused the crucial influence of aerosol coppper on HO$_2$ uptake.

At low relative humidity, the aqueous phase is highly concentrated (i.e. with a high ionic strength), and the solution is strongly non-ideal ~~which requires the activity coefficient to modify the ion concentration. Therefore,~~, consequently the activity coefficient and *salting out* effect must be taken into account for calculation of aerosol chemistry. ~~Ion~~The ion activity coefficient refers to the effective concentration of ions participating in an electrochemical reaction in an electrolyte solution.

~~Based on Ross and Noone(Ross and Noone, 1991), for an ion (Xi) of charge zi, the activity coefficient (φx) is~~ ~~$log \varphi x = -z_x^2$~~Based on Ross and Noone (Ross and Noone, 1991), for an ion (X_i) of charge z_i, the activity coefficient (φ_x) is

$$log \, \varphi_x = -z_x^2 D - \sum_y \varepsilon(x,y,I)m_y \tag{56}$$

where *D* is given by equation (7):

$$D = \frac{0.5109\sqrt{I}}{1+1.5\sqrt{I}} \tag{67}$$

~~Where~~m_y is the molality of an ion [mol ~~L~~kg^{-1}], *I* is the ~~ironic~~ionic strength of a solution[mol ~~L~~kg^{-1}], which can be calculated as follows:

$$I = \frac{1}{2} \cdot \sum m_i \cdot z_i^2 \tag{78}$$

$\varepsilon(x,y,I)$ is referred to as "interaction coefficients", and the summation extends over all ions (*y*) in the solution at a molality of m_y. For ions of similar charge, ε is set to zero. For ions of unequal charge, ε may be calculated from the mean activity

coefficient ~~loglog($A_\pm$)~~ ~~(Clegg et al., 1998)~~ (Clegg et al., 1998) of the single electrolyte (~~loglog~~$log(A_\pm)$) at the same I ~~where~~

880 according equation (9):

$$\varepsilon(x,y,I) = \frac{(\text{-}log(A_\pm)+z_xz_yD)(z_x+z_y)^2}{4I} \qquad (8 \qquad\qquad \frac{(log(A_\pm)+z_xz_yD)(z_x+z_y)^2}{4I}$$

$$(9)$$

In the ~~bulk~~condensed phase of aerosol particle, the effective molality of an ion x_i ($[x_i]_{equ}$) can be calculated as:

$$[x_i]_{equ} = [x_i] \times \text{\textcancel{φx}}(9 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \varphi_x$$

885 $$(10)$$

In the aerosol ~~bulk~~particle condensed phase, an effective concentration rather than the total concentration of Cu ion should be calculated in ~~HO$_2$~~catalytic aqueous ~~reaction~~reactions with HO$_2$. The effective concentration of Cu ion can be calculated as:

$$[Cu^{2+}\text{\textcancel{$] \times \varphi_{Cu^{2+}.}$}}]_{equ} = [Cu^{2+}] \times \varphi_{Cu^{2+}} \qquad\qquad\qquad\qquad (11)$$

890 where $[Cu^{2+}]$ is the aerosol condensed phase soluble copper concentration.

2.2.3 The conversion formula of $[\overline{HO_2}]$ and $[HO_{2(r)}]$

~~Gas phase HO$_2$ molecules dissolve in the bulk phase and diffuse from the surface of a particle toward the center coupled with aqueous phase reactions. We need to evaluate $[\overline{HO_2}]$, the assumed averaged steady state HO$_2$ concentration over the volume of particle. $[HO_{2(r)}]$ is HO$_2$ concentration at the surface. The ratio of these two concentration can be calculated~~
895 ~~as(Schwartz and Meyer, 1986):~~

~~$\frac{[\overline{HO_2}]}{[HO_{2(r)}]}$~~Gas phase HO$_2$ molecules dissolve in the particle condensed phase and diffuse from the surface of a particle toward the center in parallel with aqueous phase reactions. We need to evaluate $[\overline{HO_2}]$, the assumed averaged steady-state HO$_2$ concentration over the volume of the particle. $[HO_{2(r)}]$ is HO$_2$ concentration at the surface of particles. The ratio of these two concentrations can be calculated as (Schwartz, 1986;Schwartz, 1984):

900 $$\frac{[\overline{HO_2}]}{[HO_{2(r)}]} = 3 \times \left(\frac{coth(q)}{q} - \frac{1}{q^2}\right) \qquad\qquad\qquad (\text{\textcancel{10}}12)$$

where q is given by equation (13):

$$q = \text{\textcancel{r_p}}R_d \times \left(\frac{k_{eff}}{D_{aq}}\right)^{0.5}$$

$$(\text{\textcancel{11}}13)$$

~~Where the r_p means the geometer mean radius of the particle[cm],~~and D_{aq} is the aqueous phase diffusion coefficient [cm^{2}s^{-1}~~]~~].
905 k_{eff} is the comprehensive reaction rate coefficient which encompasses both HO$_2$ dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO$_2$ uptake process. In the copper-doped aerosol particle, because of the high value of k_{eff} and small ~~equivalent particle radius~~Count Median Diameter (R_d) (usually smaller than ~~250nm~~1 μm), the ratio is

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approximately equal to 1 (higher than 0.95 at 200nmclose to 1. At a diameter particle based onof 1 μm, and a relative humidity between 40% and 90%, the condensed phase copper ion concentration varies from 10^{-5} to 1M, the calculation) .average ratio of the surface HO_2 concentration and the condensed phase HO_2 concentration is 0.89. At 400nm diameter particles for $RH =$ 40% to 90%, the ratio is larger than 0.95. The ratios are calculated by simulation of k_{eff} and the accordingly calculations by Equation (12) and (13). Thus, in this model, we assume the surface concentration of HO_2 equals to the bulkcondensed phase average HO_2 concentration.

2.3 Laboratory results for the HO₂ accommodation coefficient

For the uptake coefficients measured at Leeds for $RH = 43\%$ reported here, the aerosol flowtube laser-induced fluorescence apparatus has been described in detail, for example in George et al. (2013) and Lakey et al. (2016b).

The accommodation coefficient of HO_2 used in the model was determined for copper-doped inorganic aerosol inparticles using values taken from various previous lablaboratory studies. The accommodation coefficient α of HO_2 (α_{HO_2}) is approximately 0.5 in sulfate aerosol and even higher for chlorine or nitrate aerosol because of the catalysiscatalytic effect of Cu^{2+} on aqueous HO_2/O_2^- (Table 1). In this situation, the aqueous reactions are fast enough thatfor the uptake process isbe limited primarily by the mass transport process (accommodation).

With the wide distribution of Cu(II)Cu^{2+} in aerosol particles, a high accommodation coefficient of HO_2 presents the possibility of HO_2 uptake as an important sink of the HO_x radicalradicals. According to existing research results, the upper limitation of α_{HO_2} with aqueous sulfate aerosol particles is around 0.5. Thus the MARK model typically selects the accommodation coefficient $\alpha\alpha_{HO_2}$ as 0.5.

Table 1: γ_{HO_2} determined under lablaboratory conditions for Cu(II)copper-doped inorganic aerosols.

Aerosol type	RH/%	Estimation of [Cu] in aerosolM (mol L^{-1})	$\alpha\alpha_{HO_2}$	Ref.
NH₄HSO₄	75%	0.0059~ −0.067*	0.40±0.21	Mozurkewich et al.(Mozurkewich et al., 1987)(Mozurkewich et al., 1987)
(NH₄)₂SO₄	45%	0.385	0.53±0.1213	Taketani et al.(Taketani et al., 2008b)(Taketani et al., 2008)
(NH₄)₂SO₄	42%	0.16	0.5±0.1	Thornton and Abbatt(Thornton and Abbatt, 2005)(Thornton and Abbatt, 2005)

(NH$_4$)$_2$SO$_4$	~~55~~53–65%	0.~~3~~45–0.7[*]	0.~~5~~4±0.3	~~Moon(Moon et al., 2018)~~(George et al., 2013)
(NH$_4$)$_2$SO$_4$	~~53~~~65%	0.~~5~~~0.7~~5~~7	0.4~~2~~6±0.~~2~~02	~~George et al.(George~~Lakey et al., ~~2013~~2016b)
(NH$_4$)$_2$SO$_4$	51%	0.0027	0.096±0.024	(Zou et al., 2019)
(NH$_4$)$_2$SO$_4$	43%	0.38	0.355±0.023	This work
NaCl	53%	~0.5	0.65±0.17	~~Taketani et al.(Taketani et al., 2008b)~~(Taketani et al., 2008)
KCl	75%	5% of KCl solution	0.55±0.19	~~Taketani et al.(Taketani et al., 2009)~~(Taketani et al., 2009)
LiNO$_3$	75%	0.03~~~ ~~–0.~~063~~0063[*]	0.94±0.5	~~Mozurkewich et al.(Mozurkewich et al., 1987)~~(Mozurkewich et al., 1987)

2.4 Reaction mechanism and reaction rate constant

The gas phase chemical mechanism of MARKM is version 2 of Regional Atmospheric Chemical Mechanism (RACM2)(Goliff and Stockwell, 2008;Goliff et al., 2013), and the aqueous chemical mechanism is based on version 2.4 of Chemical Aqueous Phase Radical Mechanism (CAPRM2.4)(Ervens et al., 2003) and updated according to that of Schwartz(Schwartz and Meyer, 1986) and Jacob(Jacob, 2000). The reaction rate constants and Henry's law constants are summarized below.

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Table 2: Kinetic data for the simulation of reactions in aqueous aerosols

No.	Reactions	K$_{298}$	E$_a$
R1	$Cu^+ + HO_{2(aq)} \rightarrow Cu^{2+} + H_2O_{2(aq)}$	2.2×10^9	
R2	$Cu^+ + 2H^+ + O_2^- \rightarrow Cu^{2+} + H_2O_{2(aq)}$	9.4×10^9	
R3	$Cu^+ + OH_{(aq)} \rightarrow Cu^{2+} + H_2O_{2(aq)}$	3×10^9	
R4	$Cu^+ + O_{2(aq)} \rightarrow Cu^{2+} + O_2^-$	4.6×10^5	
R5	$Cu^+ + H^+ + O_{3(aq)} \rightarrow Cu^{2+} + O_{2(aq)} + OH_{(aq)}$	3×10^7	
R6	$Cu^+ + H_2O_{2(aq)} \rightarrow Cu^{2+} + OH_{(aq)} + OH^-$	7×10^3	
R7	$Cu^+ + SO_4^- \rightarrow Cu^{2+} + SO_4^{2-}$	3×10^8	
R8	$Cu^{2+} + HO_{2(aq)} \rightarrow Cu^+ + H^+ + O_{2(aq)}$	$1 \times 10^{8*}$	
R9	$Cu^{2+} + O_2^- \rightarrow Cu^+ + O_{2(aq)}$	$8 \times 10^{9*}$	
R10	$O_2^- + O_{3(aq)} \rightarrow O_{2(aq)} + O_3^-$	$1.5 \times 10^{9*}$	2200^*

R11	$2HO_{2(aq)} \longrightarrow H_2O_{2(aq)} + O_{2(aq)}$	8.3×10^5	2720
R12	$HO_{2(aq)} + O_2^- \longrightarrow H_2O_{2(aq)} + O_{2(aq)} + OH^-$	9.7×10^7	106
R13	$HO_{2(aq)} + OH_{(aq)} \longrightarrow O_{2(aq)}$	1×10^{10}	
R14	$O_2^- + OH_{(aq)} \longrightarrow O_{2(aq)} + OH^-$	1.1×10^{10}	2120
R15	$H_2O_{2(aq)} + OH_{(aq)} \longrightarrow HO_{2(aq)} + H_2O_{(aq)}$	3×10^7	1680
R16	$HSO_3^- + OH_{(aq)} \longrightarrow SO_3^-$	2.7×10^9	
R17	$OH_{(aq)} + SO_3^{2-} \longrightarrow OH^- + SO_3^-$	4.6×10^9	
R18	$HSO_3^- + NO_{3(aq)} \longrightarrow H^+ + NO_3^- + SO_3^-$	1.3×10^9	2000
R19	$NO_{3(aq)} + SO_3^{2-} \longrightarrow NO_3^- + SO_3^-$	3×10^8	
R20	$HSO_4^- + NO_{3(aq)} \longrightarrow H^+ + NO_3^- + SO_4^-$	2.6×10^5	
R21	$NO_{3(aq)} + SO_4^{2-} \longrightarrow NO_3^- + SO_4^-$	1×10^5	
R22	$NO_2^- + SO_4^- \longrightarrow NO_{2(aq)} + SO_4^{2-}$	7.2×10^8	
R23	$O_{3(aq)} + SO_{2(aq)} \longrightarrow HSO_4^- + H^+ + O_{2(aq)}$	2.4×10^4	
R24	$HSO_3^- + O_{3(aq)} \longrightarrow H^+ + O_{2(aq)} + SO_4^{2-}$	3.7×10^5	5530
R25	$O_{3(aq)} + SO_3^{2-} \longrightarrow O_{2(aq)} + SO_4^{2-}$	1.5×10^9	5280
R26	$HSO_4^- + OH_{(aq)} \longrightarrow SO_4^-$	3.5×10^5	
R27	$2SO_4^- \longrightarrow S_2O_8^{2-}$	6.1×10^8	840
R28	$HSO_3^- + SO_4^- \longrightarrow H^+ + SO_3^- + SO_4^{2-}$	5.8×10^8	
R29	$SO_3^{2-} + SO_4^- \longrightarrow SO_3^- + SO_4^{2-}$	3.4×10^8	1200
R30	$H_2O_{2(aq)} + SO_4^- \longrightarrow HO_{2(aq)} + H^+ + SO_4^{2-}$	1.7×10^7	
R31	$HO_{2(aq)} + SO_4^- \longrightarrow H^+ + SO_4^{2-} + O_{2(aq)}$	3.5×10^9	
R32	$O_2^- + SO_4^- \longrightarrow O_{2(aq)} + SO_4^{2-}$	3.5×10^9	
R33	$NO_3^- + SO_4^- \longrightarrow NO_{3(aq)} + SO_4^{2-}$	5×10^4	
R34	$OH^- + SO_4^- \longrightarrow OH_{(aq)} + SO_4^{2-}$	1.4×10^7	

935 *The data is from Jacob, 2000(Jacob, 2000), others from CAPRAM 2.4(Ervens et al., 2003).

Table 3: Kinetic data for the simulation of equilibria reactions in aqueous aerosols[a]

No.	Reactions	k_{298}	E_a
E1	$H_2O_{(aq)} \longleftrightarrow H^+ + OH^-$	1.8×10^{-16}	
E2	$HO_{2(aq)} \longleftrightarrow H^+ + O_2^-$	1.6×10^{-5}	
E3	$Cu^{2+} + OH_{(aq)} \longleftrightarrow CuOH^{2+}$	1.17×10^4	
E4	$HO_{3(aq)} \longleftrightarrow H^+ + O_3^-$	5×10^{-9}	

E5	$H_2O_{(aq)} + NH_{3(aq)} \leftrightarrow NH_4^+ + OH^-$	1.17×10^{-5}	
E6	$H_2O_{(aq)} + SO_{2(aq)} \leftrightarrow HSO_3^- + H^-$	3.13×10^{-4}	
E7	$H_2O_{2(aq)} \leftrightarrow HO_2^- + H^+$	1.6×10^{-12}	-3700
E8	$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	1.02×10^9	

[a]The data is from CAPRAM 2.4(Ervens et al., 2003).

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Table 4: Kinetic data for the simulation of gas-liquid phase conversion reactions[b]

No.	Reactions	k_{298}
T1	$HO_2 \longrightarrow HO_{2(aq)}$	$k_{mtHO2} \cdot ALWC$
T2	$OH \longrightarrow OH_{(aq)}$	$k_{mtOH} \cdot ALWC$
T3	$O_3 \longrightarrow O_{3(aq)}$	$k_{mtO3} \cdot ALWC$
T4	$O_2 \longrightarrow O_{2(aq)}$	$k_{mtO2} \cdot ALWC$
T5	$H_2O_2 \longrightarrow H_2O_{2(aq)}$	$k_{mtH2O2} \cdot ALWC$
T6	$HO_{2(aq)} \longrightarrow HO_2$	$k_{mtHO2}/(H_{HO2}RT)$
T7	$OH_{(aq)} \longrightarrow OH$	$k_{mtOH}/(H_{OH}RT)$
T8	$O_{3(aq)} \longrightarrow O_3$	$k_{mtO3}/(H_{O3}RT)$
T9	$O_{2(aq)} \longrightarrow O_2$	$k_{mtO2}/(H_{O2}RT)$
T10	$H_2O_{2(aq)} \longrightarrow H_2O_2$	$k_{mtH2O2}/(H_{H2O2}RT)$

[b]The data is from Schwartz, 1986(Schwartz and Meyer, 1986)

Table 5: Henry's Law constant

No.	Species	H_{298} [M atm^{-1}]	$\Delta H/R$ [K]
1	O_3	1.14×10^{-2}	-2300
2	O_2	1.3×10^{-3}	-1700
3	HO_2	2×10^3	6600*
4	H_2O_2	7.4×10^4	6615*
5	OH	25	-5280

945 * The data is from Mao et al., 2013(Mao et al., 2013a), others from CAPRAM 2.4(Ervens et al., 2003).

*Cu concentration is in molality (mol kg^{-1}).

3 Results and Discussion

3.1 Parameter sensitivity analysis of the MARK model

Hygroscopic inorganic ~~particle is~~particles are one of the most important ~~component~~components of $PM_{2.5}$ in ~~the~~ ambient air. The annual average contribution of inorganic aerosol to $PM_{2.5}$ is between 25% and 48% across China ~~(Tao et al., 2017)~~(Tao et al., 2017), especially NH_4^+, SO_4^{2-}, NO_3^- and other inorganic ions. In ~~lab~~laboratory studies of radical heterogeneous reactions, $(NH_4)_2SO_4$ aerosol is most widely studied because of its simple components ~~and~~, easy way to generate. ~~Without the interference of organic matter, it is convenient~~ and as they are important component for urban aerosols (Cheng et al., 2012;Yin et al., 2005). A simplified approach was used to explore the mechanism of HO_2 heterogeneous uptake ~~and~~in order to derive ~~its~~a parameterized equation~~, which provides a good reference~~ for the ~~heterogeneous~~ uptake coefficient, γ_{HO_2}, and which did not consider any potential role of organic matter present in the aerosol because of the reasons detailed below.

Using laboratory measurements of γ_{HO_2} for particles containing a single organic component (Lakey et al., 2016b;Lakey et al., 2015), it was concluded that the organic content of an aerosol particle may affect several important parameters in the model. For example, the aerosol pH, hygroscopic properties of the aerosol, the rate of diffusion of HO_2 ~~in the actual~~within the aerosol and a reduction in the concentration of Cu^{2+} via the formation of complexes that could affect the ability of Cu to undergo redox reactions with HO_2 and O_2^-. Hence, it is expected that the presence of organic material would change the value of γ_{HO_2}, but incorporation of terms in the parameterisation of γ_{HO_2} from organic material is beyond the scope of this work, and should be a focus of future studies. In fact, during a recent field measurement of the urban atmosphere ~~environment.~~ using a combined laser-flash photolysis and laser-induced fluorescence (LFP-LIF) technique coupled with a versatile aerosol concentration enrichment system (VACES) in Japan, Zhou et al. showed that the average value of γ_{HO_2} was 0.24 ± 0.20 (1σ) during the study period (Zhou et al., 2020). Although conditions will be different between field locations, this "field measured" value is within the broad range of our model output that does not include organic matter effects.

In this study, $(NH_4)_2SO_4$ aerosol uptake HO_2 is simulated by the MARK model, and good correlation between simulation results and experimental results are obtained especially considering the influence of both [~~Cu~~Cu^{2+}] and *RH*.

~~Figure 1 indicates the influences of factors including aerosol mass concentration and bulk phase pH on the heterogeneous process of HO_2. As the RH rising, the γ_{HO_2} exhibits a logarithmic growth trend. Higher RH means more possibility of the aerosol to have higher water content which promotes the activities of reactant ion in the aerosol bulk and the solubility of gas phase reactant. γ_{HO_2} has an exponential growth trend of $[Cu^{2+}]$ with an effective threshold value of 10^{-4} M, exceeding which concentration, HO_2 uptake rate increases significantly. This threshold is consistent with the results of Mozurkewich, 1987(Mozurkewich et al., 1987). When the concentration of Cu(II) is high enough, the uptake coefficient is suppressed by the limitation of HO_2 solubility thus cannot reach to α.~~
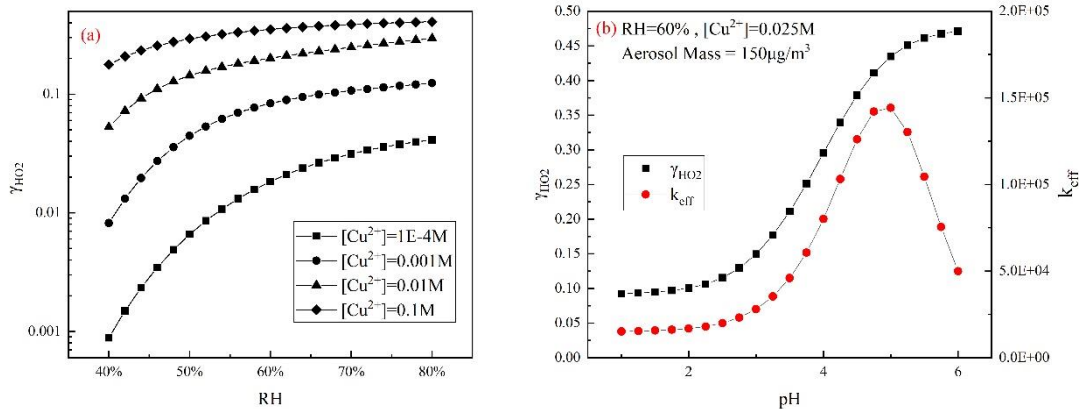
980   Figure 1 shows the influences of factors including aerosol mass concentration and condensed phase pH on the heterogeneous process of HO_2. As the *RH* rises, the γ_{HO_2} exhibits a logarithmic growth. Higher *RH* means a higher water content which dilutes the bulk phase ions thus promotes the activity coefficients of reactant ions in the aerosol particle condensed phase and the solubility of the gas phase reactant such as OH, HO_2 and H_2O_2.
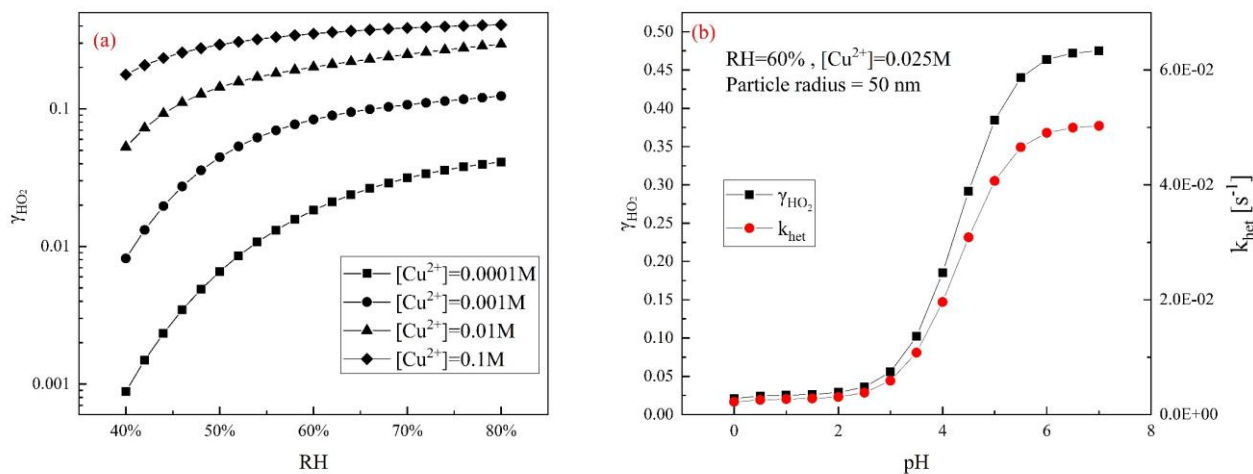
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Figure 1: ~~Parameter analysis~~Influence of various parameters upon γ_{HO_2} predicted by the ~~Mark~~MARK model. (a) γ_{HO_2} increases with the *RH* at different [Cu^{2+}]; (b)~~γ_{HO_2}~~ γ_{HO_2} ~~in~~denoted by black ~~square dotted line increases with aerosol bulk phase pH and k_{eff}~~squares and black line and k_{het} in red ~~circular dotted~~circles and red line ~~has a peak value at about pH=5 then declines quickly.~~increase with aerosol particle condensed phase pH.

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γ_{HO_2} ~~has an S~~presents a sigmoid-shaped growth with aerosol ~~bulk phase pH. k_{eff} is the comprehensive reaction rate constant of HO$_2$ dissolution equilibrium and liquid phase chemical-physical reaction during HO$_2$ heterogeneous uptake reaction.~~particle condensed phase pH. In the model, it is found that as the pH ~~rising~~rises, the uptake coefficient rises rapidly because HO$_2$ is a weak acid (*pKa* = 4.7) and has a low solubility in an acidic environment. The higher ~~bulk~~condensed phase pH is favorable for the dissolution equilibrium of the gas phase HO$_2$. ~~On the other hand~~This trend is consistent with the observed second-order rate constant of HO$_2$/O$_2^-$ reviewed by Bielski et al. 1985 (Bielski et al., 1985). Moreover, aqueous phase reaction rates of HO$_2$/O$_2^-$ and Cu^{2+}~~decrease~$^+$/Cu$^+$ increase with the increasing of ~~bulk phase pH.~~condensed phase pH because in an alkaline environment HO$_2$ is more dissociated to O$_2^-$ which has quicker reaction rate with Cu^{2+}/Cu$^+$. The pH of the ambient atmospheric aerosol is measured generally below 5 even ~~for~~when the concentration of NH$_3$ is high ~~NH$_3$ cases like~~as in Beijing and Xi'an (Ding et al., 2019;Guo et al., 2017) with a range of 3~~-6~-5. At this range, ~~HO$_2$ heterogeneous reaction~~γ_{HO_2} is highly affected by aerosol condensed phase pH ~~indicating~~may mainly because of the ~~significance of this field~~change of ~~study~~solubility.

3.2 Model ~~Verification~~Validation

~~In the existing γ_{HO_2} parameterized equation~~In this study, we used the MARK model to simulate the observed γ_{HO_2} from all the available laboratory studies, which were conducted with different ambient *RH* and Cu^{2+} concentrations (Zou et al., 2019;Lakey et al., 2016b;Thornton and Abbatt, 2005;Taketani et al., 2008~~;Hanson et al., 1992;Hanson et al., 1994;Jacob, 2000;Kolb et al., 1995~~)~~, the quasi first-order reaction rate K^I equals to $K^{II} \times [Cu]$, where K^{II} is fixed regardless of the aerosol pH, metal ion self reactions and other reagents in the bulk phase, and may thus cause deviation from the actual situations. According to the research by Bielski in 1985(Bielski et al., 1985), the secondary reaction rate K^{II} of Cu(II) and HO$_2$ in aerosol liquid phase or cloud water is 1.5×10^7 L mol^{-1}s^{-1} because of the pH limitation, and not the more commonly used value of 1×10^9 L mol^{-1}s^{-1}.~~
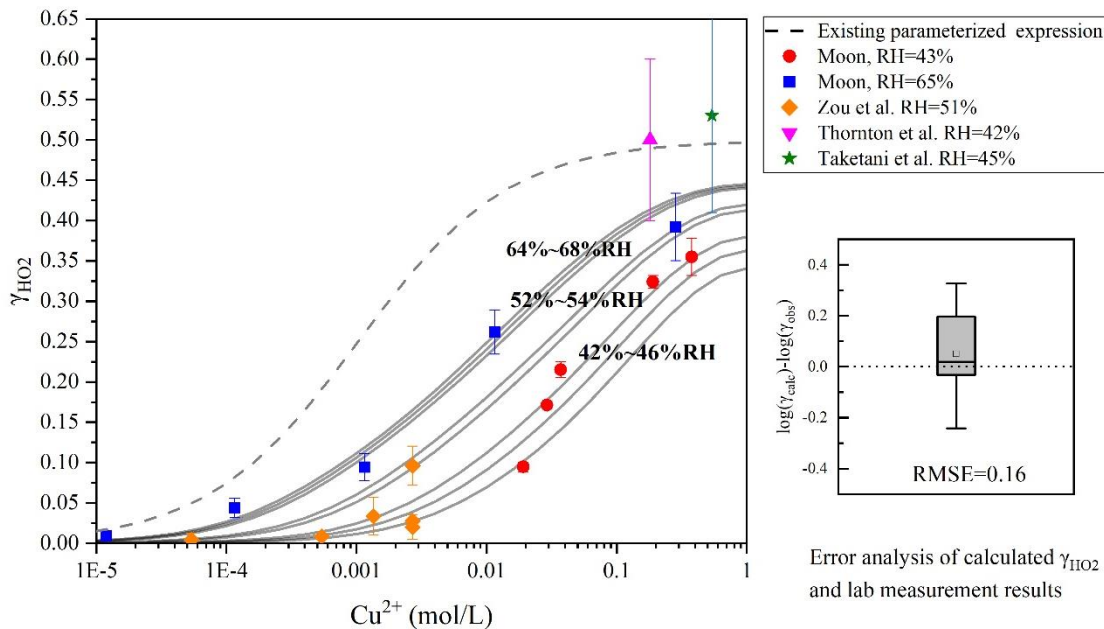
Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red circles denote the results at 43% RH, and blue squares at 65% RH (research by Moon et al., 2018(Moon et al., 2018)). Yellow diamonds denote results at 51% RH (research by Zou et al., 2019(Zou et al., 2019)), inverted triangle at 42% RH (research by Thornton et al., 2005(Thornton and Abbatt, 2005)) and star at 45% RH (research by Taketani et al., 2008(Taketani et al., 2008b)). Estimation of copper concentration is based on the analysis of Vlasenko et al., 2017(Vlasenko et al., 2017) and references in these studies. The gray dotted line denotes the current parameterized equation and the gray lines represent the model results of MARK model in this study. The root median square error (RMSE) between the modeled values and the results from Moon et al., 2018(Moon et al., 2018) and Zou et al., 2019(Zou et al., 2019) is 0.16 indicating a small deviation in MARK model calculations.

−. In general, good agreement is achieved between the MARK model results and the results of the previous laboratory studies, which were also classified based on a statistical parameter: root mean square error (RMSE) (Figure 2).
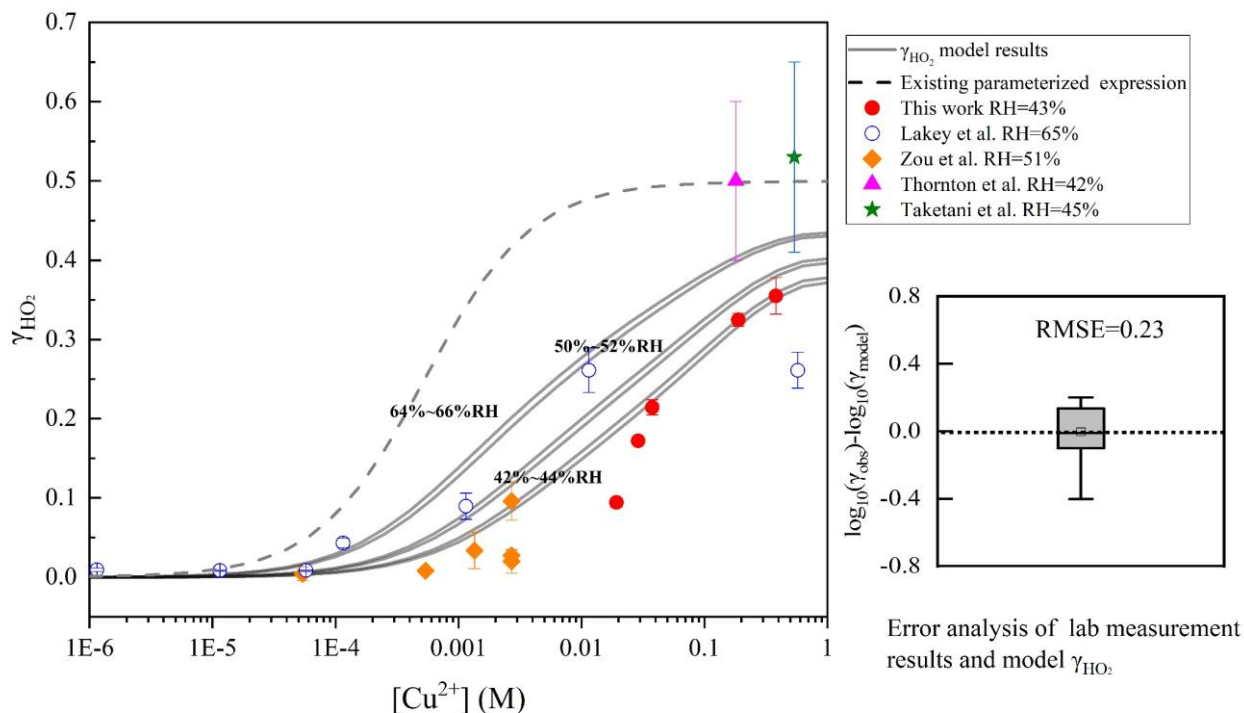
Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red filled circles denote the results at 43% *RH* measured at Leeds. Blue hollow circles at 65% *RH* (Lakey et al., 2016b). Yellow filled diamonds denote results at 51% *RH* (Zou et al., 2019), filled purple triangle at 42% *RH* (Thornton and Abbatt, 2005) and filled green star at 45% *RH* (Taketani et al., 2008). The grey dotted line denotes the current parameterized equation (Thornton et al., 2008;Hanson et al., 1992;Hanson et al., 1994;Jacob, 2000;Kolb et al., 1995) and the solid grey lines represent the model results of the MARK model in this study at various *RH* (two lines represent the range of *RH* from 64% to 66%, 50% to 52% and 42% to 44%). The root mean square error (RMSE) between the MARK modelled values and the full dataset (0.23). The aerosol pH is set as 4.5 based on the aqion 7.0.8 interface considering the participation of Cu ion (for details please see https://www.aqion.de/).

As shown in Fig. 2. when the ~~aerosol~~condensed phase copper ion concentration is less than ~~1~~-2×~~10⁴M~~10⁻⁴ M, the heterogeneous uptake of HO₂ is not significant. This threshold is consistent with the results of previos researches (Mozurkewich et al., 1987;Lakey et al., 2016b). As the copper concentration increases, γ_{HO_2} rapidly rises to the ~~limits~~limit of the accommodation ~~and~~coefficient determined by the HO₂ solubility. Many research studies have proposed that ambient *RH* affects γ_{HO_2} (Thornton ~~and Abbatt, 2005;Thornton~~ et al., 2008;Taketani et al., ~~2008b~~2008, 2009;Taketani and Kanaya, 2010;Taketani et al., 2012;Matthews et al., 2014;Thornton and Abbatt, 2005). For hygroscopic inorganic aerosols, *RH* significantly affects the aerosol liquid water content, changing its ionic strength, aqueous reagent concentrations, and the effective Henry's coefficient.

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~~In this study, we used MARK model to simulate the observed γ_{HO_x} from all the available lab studies, which were conducted with different ambient RH and Cu²⁺ concentrations~~The deviation of γ_{HO_2} between the MARK model and laboratory studies is smaller than the predicted results from the existing parameterized equation ~~(Moon et al., 2018;Zou et al., 2019)~~(Thornton et al., 2008;Hanson et al., 1992;Hanson et al., 1994;Jacob, 2000;Kolb et al., 1995;Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.). ~~In general, good agreement is achieved between the MARK model results and the results of the previous lab studies, which were also classified based on a statistical parameter: root mean square error (RMSE). The γ_{HO_x} from both the MARK model and lab studies are much smaller than the predicted results from the existing parameterized equations for [Cu²⁺] (smaller than 0.1 mol L⁻¹). Therefore, a novel parameterized equation is required to better describe the influence of [Cu²⁺] on γ_{HO_x}.~~

as shown in Figure 2. In order to reduce the overestimation of the existing parameterized equation, we used the effective rate constant of HO_2 (O_2^-) with Cu ions as 1.5×10^7 $M^{-1} s^{-1}$ rather than the more commonly used value of 1×10^9 $M^{-1} s^{-1}$ according to the research by Bielski in 1985 (Bielski et al., 1985) considering the pH limitation (pH is about 3-5 in ambient aerosol particle condensed phase as dicussed above). The prior value (1.5×10^7 $M^{-1} s^{-1}$) reflects the rate of reaction between HO_2 and Cu^{2+}, more prevalent in acidic aerosol such as ammonium sulphate, and the latter between O_2^- and Cu^{2+} ions, which is more prevalent in aerosols with a pH greater than the pK_a of HO_2, such as NaCl (Bielski et al., 1985). This treatment within the calculation can bring predictions more in line with experimental results compared to the high value of 1×10^9 L $mol^{-1} s^{-1}$ used in the existing parameterized equation. IUPAC (Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.) proposed the effective rate coefficient for the reaction of HO_2 (O_2^-) with Cu ions as 5×10^5 $M^{-1} s^{-1}$ to achieve the best fit based on the calculation results from Lakey et al. (2016b). This assumption is not in accordance with the aqueous reaction rate coefficient from other databases mentioned below, and needs further laboratory measurements to confirm it. According to the aqueous reaction rate coefficient from NIST and the latest measurement result (Lundström et al., 2004;Huie, 2003), the rate coefficient of HO_2 with Cu^{2+} is 1×10^8 or 1.2×10^9 $M^{-1} s^{-1}$ at pH= 2 and pH=1, respectively. These two rate coefficients were quantified in a low pH environment (pH=2 for 1.2×10^9 $M^{-1} s^{-1}$ and pH=1 for 1×10^8 $M^{-1} s^{-1}$). At the same time, the reaction rate of O_2^- with Cu^{2+} is 8×10^9 $M^{-1} s^{-1}$ for pH in the range 3-6.5 (Huie, 2003). At higher pH, the reaction rate of HO_2 with Cu^{2+} may change, but it is unknown whether it will decrease by four orders of magnitude. Further kinetics experiments are needed at varying pH to verify the reaction rate coefficient of Cu^{2+} ions with HO_2 and O_2^- in aqueous solution. The rate constants used in the MARK model are shown in the Table S. 1 in the SI. The main reason for the differences between the original parameterization and the MARK model is the effect of including the activity coefficients of Cu ions and HO_2 and the effects of reactions of different valence states of copper ions. Considering the small RMSE between the MARK model and the laboratory studies, we proposed a novel parameterized equation to better describe the influence of [Cu²⁺] on γ_{HO_2}.

3.3 A novel parameterized equation ~~for~~of γ_{HO_2}

When the full reaction system reaches steady-state, the reaction of HO_2 in the aqueous particle phase can be expressed as the following ~~equation~~reaction scheme (Schwartz, 1984;Schwartz and ~~Meyer, 1986;Schwartz and~~ Freiberg, 1981;Schwartz, 1987)

$$HO_{2(g)} \rightleftharpoons HO_{2(r)} \rightleftharpoons HO_{2(a)} \xrightarrow{k_{eff}} Products \tag{~~12~~14}$$

Gas phase $HO_{2(g)}$ molecule transports onto the surface of the aerosol particles $HO_{2(r)}$ then dissolves at the ~~bulk~~condensed phase to give $HO_{2(a)}$. ~~Because the reaction~~The reactions between ~~[~~ Cu^{2+} ~~]~~$^+$/Cu^+ and HO_2 ~~is a~~ can be seen as catalytic ~~reaction,~~reactions, because in the model simulations, the total amount of ~~[Cu^{2+}] concentration in the system~~$[Cu^{2+}]+[Cu^+]$ does not change with reaction time. ~~The rate of HO_2 aqueous reaction with copper ions is noted as k_{eff}.~~For fine particles, we can safely assume that the interface concentration ~~[HO_2]~~$[HO_{2(r)}]$ is equal to the ~~bulk~~condensed phase average $\overline{[HO_2]}$ concentration due to rapid diffusion in the liquid phase (details have been dicussed ~~above). With~~in section 2.2.3). For the submicrometer aerosol particles with which most uptake reaction occurs, the influence of the gas phase diffusion limitation can be neglected. Hanson et al. (1994) proposed the definition of the uptake coefficient as $\gamma = \alpha(1 - \frac{c_{a,surf}}{H^{cc}c_{g,surf}})$ ~~,~~ where $c_{a,surf}$ is the suface concentration of the reactant, $c_{g,surf}$ is the gas phase concentration. In the process of HO_2 uptake, we deduce the parameterized equation of γ_{HO_2} in the framework of the resistance model. ~~For the submicrometer Cu(II) doped particles with which most uptake reaction occurs, the influence of the gas phase diffusion limitation can be neglected.~~:

$$\frac{1}{\gamma} = \frac{1}{\alpha_{HO_2}} + \frac{3 \times v_{HO_2}}{4 \times R_d \times H_{corr} \times RT k_{eff}} \tag{15}$$

$$k_{eff} = f(ALWC, PM) \times [Cu^{2+}]_{equ} \tag{16}$$

$$f(ALWC, PM) = 10^6 \times (5.87 + 3.2 \times ln(ALWC/[PM] + 0.067) \times [PM]^{-0.2} \tag{17}$$

$$[Cu^{2+}]_{equ} = [Cu^{2+}]^{\varphi} = [Cu^{2+}]^{0.65} \tag{18}$$

From Eq. (15), it can be deduced that γ_{HO_2} can be calculated by optimizing k_{eff} under different ambient environmental conditions. ~~The MIPFIT model~~The MIPFIT model (Markwardt, 2009;Lewis et al., 2009) in the IDL software program is used to optimize k_{eff} using the Levenberg-Marquardt algorithm. Because the equation is empirical, the initial value of k_{eff} is set as 1. ~~From Eq. (14), it can be deduced that γ_{HO_x} can be calculated by optimizing k_{eff} under different ambient environmental conditions. k_{eff} is related to the aerosol bulk~~condensed ~~phase soluble copper concentration [Cu^{2+}] with an exponential relationship to the parameterization of the catalytic reactions, which is denoted in Eq. (17~~16~~). The exponent of [Cu^{2+}] is globally fitted using the MIPFIT method. It is found that the overall R^2 is higher than 0.97 and the residual is minimized when the exponent is 0.65. $f(ALWC, [PM])$ has a negative exponential relationship to [PM], and has a positive linear relationship to RH.~~

~~$$k_{eff} = k^{cat} \times [Cu^2 +]_{equ} \tag{13}$$~~

~~where k^{cat} is the pseudo effective catalytic rate, $[Cu^{2+}]_{equ}$ is the equivalent concentration of Cu, And γ_{HO_x} can be expressed as~~

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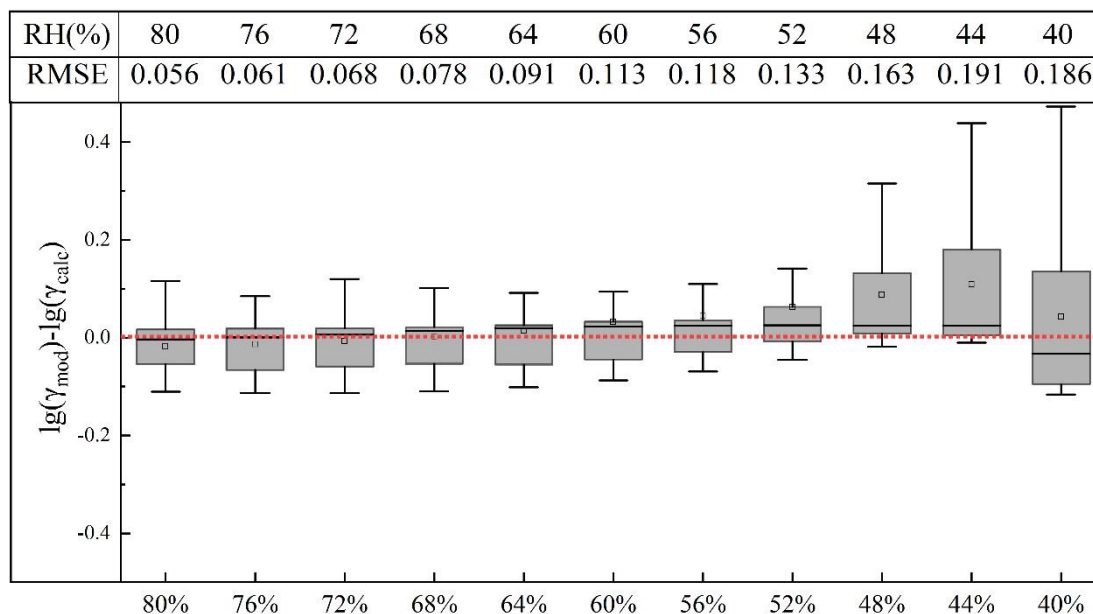$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{3 \times \upsilon}{4 \times R_d \times H_{corr} RT k_{eff}} \tag{14}$$

$$k_{eff} = f(\text{ALWC}, \text{PM}) \times [Cu^{2+}]_{equ} \tag{15}$$

$$f(\text{ALWC}, \text{PM}) = 10^6 \times (5.87 + 3.2 \times ln(\text{ALWC}/[\text{PM}] + 0.067) \times [\text{PM}]^{-0.2} \tag{16}$$

$$[Cu^{2+}]_{equ} = [Cu^{2+}]^{\varphi} = [Cu^{2+}]^{0.65} \tag{17}$$

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We further calculated the RMSE of the modeled data and parameterized equation (15) data under different *RH* conditions.

1110 The range of values shows the difference between the modeled data and parameterized equation data at different Cu^{2+} concentration. At low *RH* and consequently relatively low ALWC, γ_{HO_2} is more sensitive to $[Cu^{2+}]$ expecially at low $[Cu^{2+}]$ ($<10^{-4}$M). This sensitivity can not be fully represented in the parameterized equation. What is more, at low $[Cu^{2+}]$ and low *RH*, the value of γ_{HO_2} is smaller than in other conditions, so that the uncertainty of γ_{HO_2} becomes larger.

All the RMSE values are ~~less~~smaller than 0.2, which indicates a minor deviation from the laboratory results in our γ_{HO_2}

1115 equation. ~~Under~~In the typical ambient urban atmospheric environment, with an aerosol mass concentration of 10~~-~~–300 μg m$^-$ ^{3}, aqueous Cu^{2+} concentration of 10^{-5}~~-~~–1M, and a relative humidity between 40~~%~~%~–90%, the parameterized equation can be used ~~based on the comparison. For dry conditions where RH% is less than 40%, the equation was not tested due to the lack of lab and model studies.~~. The HO$_2$ uptake under dry conditions needs further investigation in the future, but probably is not of high priority because the effective reaction volume becomes 10% or less of the aerosol volume for dry conditions and the HO$_2$

1120 uptake may then be neglected for typical tropospheric conditions (Taketani et al., ~~2008b~~2008;Kanaya et al., 2009;Taketani and Kanaya, 2010;Thornton et al., 2008;~~Thornton and Abbatt, 2005~~George et al., 2013).

RH(%)	80	76	72	68	64	60	56	52	48	44	40
RMSE	0.056	0.061	0.068	0.078	0.091	0.113	0.118	0.133	0.163	0.191	0.186

RH(%)	80	76	72	68	64	60	56	52	48	44	40
RMSE	0.056	0.061	0.068	0.078	0.091	0.113	0.118	0.133	0.163	0.191	0.186

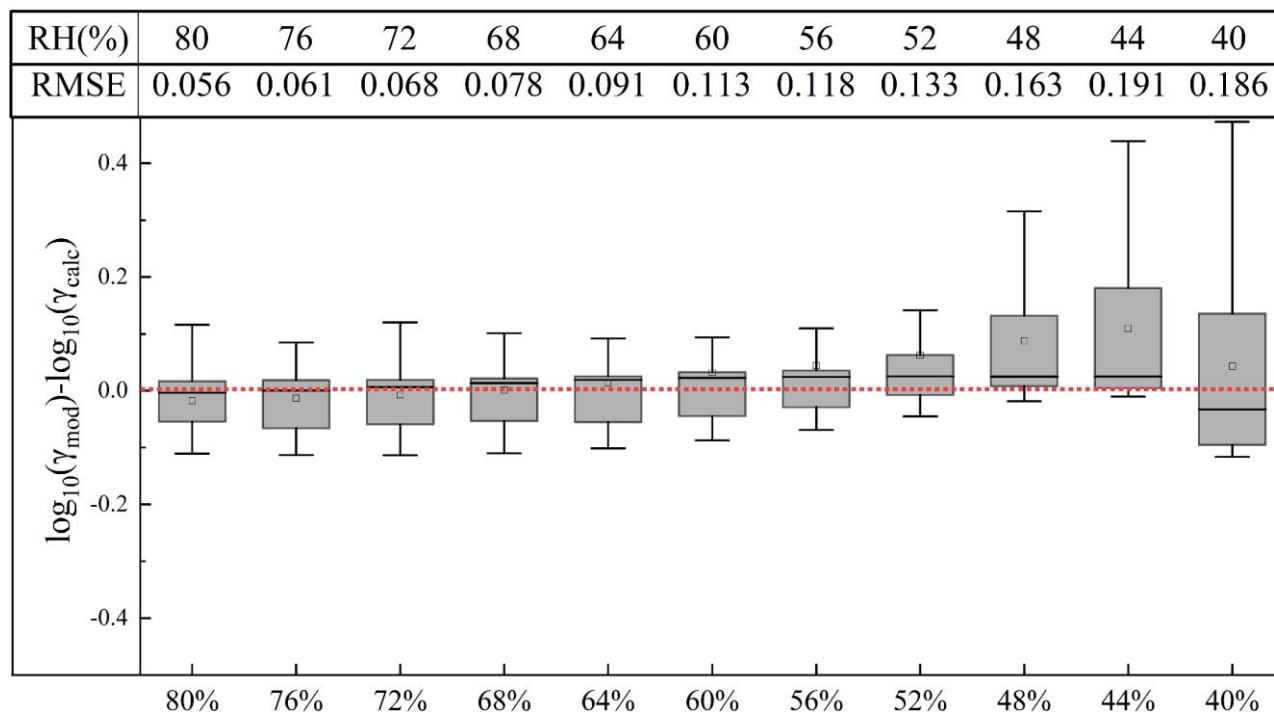Figure 3: Comparison of the <u>MARK</u> modeled γ_{HO_2} <s>and</s><u>to the</u> corresponding calculated values from the new parameterized equation<s>.</s> <s>$\log_{10}$ (15).</s> log_{10}($\gamma_{\overline{mod}}$$\gamma_{mod}$) is the logarithmic value of modeled γ_{HO_2} and <s>$\log_{10}$</s>log_{10}($\gamma_{\overline{cal}}$$\gamma_{cal}$) is the calculated value from the new parameterized equation<s>.</s> <u>(15).</u>

3.4 <s>Impact</s><u>Evaluation</u> of the <u>impact of the new</u> HO₂ uptake <s>evaluated with the novel parameterized equation</s><u>parametrization in the Wangdu campaign</u>

Many model studies <u>(</u>Lakey et al., 2015;Mao et al., 2013b;Martinez et al., 2003;Tie et al., 2001<u>;Whalley et al., 2015</u>) suggest that heterogeneous uptake of HO₂ radical affects the global distribution of trace gases and the <s>atmosphere</s><u>atmospheric</u> oxidant capacity especially in regions with high aerosol loading or low NOx concentration. The importance of aerosol chemistry as a sink for ozone precursors in North China Plain has been suggested in many model studies <u>(</u>Li et al., 2019b;Lou et al., 2014). The competition of HO₂ with aerosol and gas phase reactants is crucial when evaluating the influence of heterogeneous reactions on the atmospheric oxidant capacity.

Based on the results of a comprehensive field campaign performed in summer 2014 in a rural site (Wangdu) in the North China Plain<s>, HO₂ uptake</s> <u>(</u>Tan et al., 2020), the HO₂ uptake coefficient and the ratios of the HO₂ uptake <u>loss</u> rates (TR$_{HO2uptake}$) to the sum of the ROx termination rates <u>(</u>TR$_{ROxsinks}$) are calculated with direct measurements of the ROx radicals, trace gas <s>compounds</s><u>species</u>, ALWC and the aerosol <s>properties.</s><u>condensed phase component concentrations (please see the SI for details).</u> The experimental determined ROx termination rates include reaction channels from OH + NO₂<s>/</s><u>,</u> <u>OH +</u> NO, HO₂ +

1140 HO$_2$, HO$_2$ + RO$_2$, and RO$_2$ + NO. Considering the solubility and size distribution of ~~aerosol~~particle metal copper (Fang et al., 2017;Hsu et al., 2010a;Mao et al., 2013a) we can estimate γ_{HO_2} in daytime and night. ~~Effective soluble Cu^{2+} used in the calculation is 25% of total aerosol metal copper concentration.~~

3.4.1 Average results of observed meteorological parameters and trace gases concentration in the Wangdu campaign

Wangdu is located in the center of the Beijing-Tianjin-Hebei area and is a regional site. The observation was carried out in
1145 the summer with serious photochemical smog ~~pollutions(Tan et al., 2017). The table~~pollution events (Tan et al., 2017;Tan et al., 2020). Table 2 summarizes the meteorological and chemical conditions in this field campaign. In terms of parameters such as temperature, pressure and humidity, the ~~Wandu~~Wangdu area is a high-temperature and high-humidity ~~stage~~environment with a monsoon climate.

1150 Table ~~6~~2: Average daytime results of observed meteorological parameters and trace gases concentration in Wangdu campaign from June 10th , 2014 to July 6th ,2014.

~~Wangdu~~Parameters	Average ~~results~~values	1σ Accuracy
Temperature /°C	27±4	±0.05%
Pressure /hPa	1000±5	±0.05%
RH/%	~~58~~61±18	±0.05%
O$_3$/ppb	55.6±9.0	±5%
NO$_x$/ppb	10±13.6	±20%
HONO/ppb	0.8±0.24	±20%
CO/ppm	0.6±0.19	<5%
Isoprene/ppb	0.5±0.11	±15%-20%
HCHO/ppb	7±0.69	±5%

3.4.2 Calculation of ~~aerosol liquid water content (ALWC) in Wangdu campaign~~

~~Assuming aerosol particles are all spherical, particle total surface area (S) can be calculated as:~~

$$S = \int \frac{dN}{dlogD_p} \cdot \pi D_p^2 \cdot dlogD_p \tag{18}$$

1155 ~~Where, $\frac{dN}{dlogD_p}$ is particle number size distribution, and D_p is particle diameter.~~

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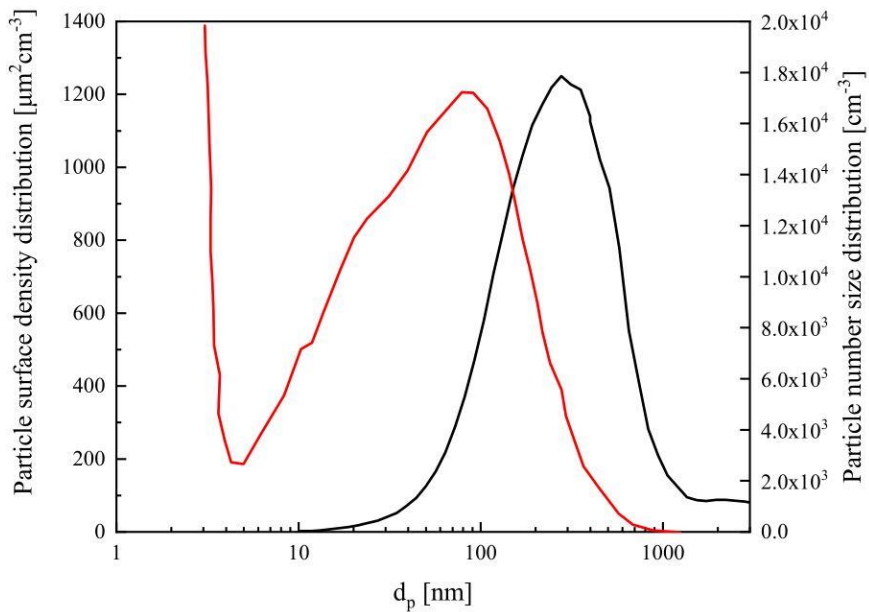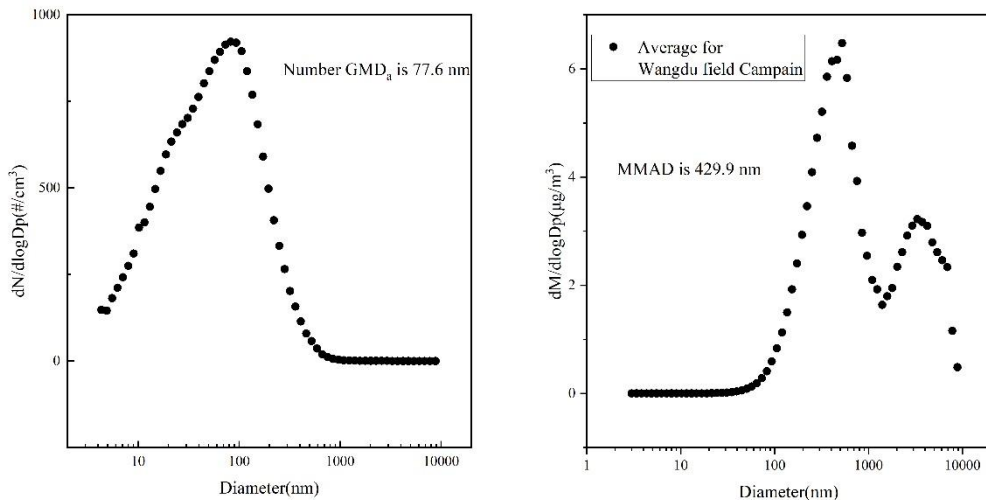
Figure 4: PSSD (black line) and PNSD (red line) of aerosol in Wangdu field campaign

Figure 5: Aerosol number distribution and mass distribution in Wangdu field campaign

Figure 4 shows the dry state average particle number size distribution (PNSD) and particle surface size distribution (PSSD) for the whole campaign. The peak diameter of PSSD is around 300 nm, which is much higher than that of PNSD. The uncertainty of the calculated aerosol surface concentrations S is estimated to be 10%.

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~~The size-resolved κ is estimated based on real time measurement of HHTDMA. In case the HHTDMA data is not available, the campaign average of HHTDMA data will be used. Having size-resolved κ, the wet diameter of particles with any dry diameter can be calculated with κ-Köhler function(Khvorostyanov and Curry, 2007). And the total surface area S can be calculated with Eq. (19). For a known T and S, the relationship between κ the hygroscopic growth factor $g(D_p, RH)$ at a certain diameter Dp and a certain RH, can be calculated. With the assumption of the conservation of volume during aerosol hygroscopic process, the volume of ALWC is equal to subtract the volume of dry aerosol particles from that of wet particles. Using the size-resolved hygroscopic growth factors and the PNSD measurement, the ALWC can be calculated:~~

$$\text{ALWC} = \left[\frac{\pi}{6}\sum_t N_t D_{p,t}^3 \left(g(D_p, RH)^3 - 1\right)\right]\rho_w \qquad (19)$$

~~Where N_t represents the number concentration of dry particles of the ith bin, $D_{p,t}$ is the particle diameter of that bin, ρ_w is the density of water.~~

~~3.4.3 Calculation of~~ soluble copper ion concentration

For particle radius smaller than $2.5\mu m$, which are the most contributing bins of aerosols in HO_2 uptake, the mass fraction of Cu is about 33%~100% in four size bins in ambient aerosols (<1μm, 1-2.5 μm, 2.5-10 μm, >10μm) (Mao et al., 2013a). During this campaign, the total concentration of heavy metal ions in fine particles (smaller than $2.5\mu m$) was measured using a commercial instrument based on non-destructive X-ray fluorescence technique (Xact 625, Cooper Environmental). Since the concentration of soluble copper concentration rather than total copper concentration is used in the model, it is necessary to analyze the ratio of soluble copper to total copper in the aerosol particles. According to ~~the~~previous research results, ~~it is found that~~ the dissolution ratio of copper in aerosol particles varies from ~~40~~20% to ~~60~~70% in different regions, being solubility lower in smaller particles (Fang et al., 2017;Hsu et al., 2004;Hsu et al., 2010b).

~~During this campaign, the total concentration of heavy metal ions in fine particles was measured using a commercial instrument based on nondestructive X-ray fluorescence technique (Xact 625, Cooper Environmental).~~ Therefore, when using the empirical ~~formula~~paraterization equation (Eq.15) to calculate the HO_2 heterogeneous uptake coefficient, it is necessary to reduce the copper concentration ~~by 40% to 60%. And for particle radius smaller than 1μm, which are the most contributing bins of aerosol in HO_2 uptake, Cu fraction is about 25%~71%(Mao et al., 2013a).~~considering the solubility and the distribution in the accumulation mode of aerosol particles. We take 50% copper is soluble in the particle condensed phase and 50% copper is in the accumulation mode. Thus we assume 25% of total aerosol metal copper concentration is soluble in the accumulation mode when calculating γ_{HO_2} in Wangdu campaign. The aerosol liquid water content is divided by the hourly resolution total copper concentration (ng m^{-3}) and the atomic mass of copper (64) to obtain the total copper ~~molality~~molarity in the aerosol (mol L^{-1} ~~H$_2$O). The calculated average soluble Cu ion molality in accumulation mode of aerosol ranging from 0.003 to 0.012 M in Wangdu campaign. The uncertainty of the concentration of copper ion will be discussed later.~~).

3.4.~~4~~3 γ_{HO_2} estimated at Wangdu field campaign

By inputting the soluble copper concentration, aerosol mass concentration, aerosol particle ~~geometer~~geometric mean diameter and the corresponding relative humidity and temperature into the empirical equation, we can obtain ~~the~~an estimation of γ_{HO_2} in ~~Wangdu~~ suburban Wangdu, which is shown in Fig.~~6~~ 4 (a) and (b). The ~~valid data points are 224 with a~~ time resolution ~~of~~is 1 hour. The aerosol pH is calculated using the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007). Average aerosol mass concentration is 67.2±39.7 μg m^{-3}, the average Cu concentration is 35.8±57.7 ng m^{-3}. ~~he GaussAmpfitting shows the median~~ The results of a fit to a GaussianAmp function results in a γ_{HO_2} ~~is~~median value of 0.109~~±~~ ± 0.~~005~~045 in daytime and 0.~~139~~130±0.~~007~~053 at night in the Wangdu campaign~~.~~ (γ_{HO_2} will increase 1.57 times from 0.075±0.031 at 10% solubility to 0.193±0.079 at 70% solubility for the summary of day and night data).

Tan et al. (2017) had compared the measured and modelled OH, HO$_2$ and RO$_2$ radicals in the Wangdu campaign. However, in this paper, they did not discuss the influence of HO$_2$ uptake. A very recent publication (Tan et al., 2020) calculated γ_{HO_2} in the Wangdu campaign based on the comparison of field measurement data for HO$_2$ and concentrations calculated by the box model. The paper proposes that all γ_{HO_2} calculated in this way from the Wangdu campaign can be fitted to a Gaussian distribution around the value of 0.08 ± 0.13. This value is similar to our estimation in this paper considering the indirect measurement uncertainty (please see the SI).

The experimentally determined ROx termination rates include reaction channels from OH + NO$_2$, OH + NO, HO$_2$ + HO$_2$, HO$_2$ + RO$_2$, RO$_2$ + NO. The ratio (R_1) of HO$_2$ uptake loss rate ($L_{HO2uptake}$) to the whole RO$_x$ loss rate (L_{ROx}) is calculated by Equation (20) and (21).

$$L_{HO2uptake} = 0.25 \cdot v_{HO_2} \cdot [ASA] \cdot [HO_2] \tag{20}$$

$$R_1 = \frac{L_{HO2uptake}}{L_{ROx}} \tag{21}$$

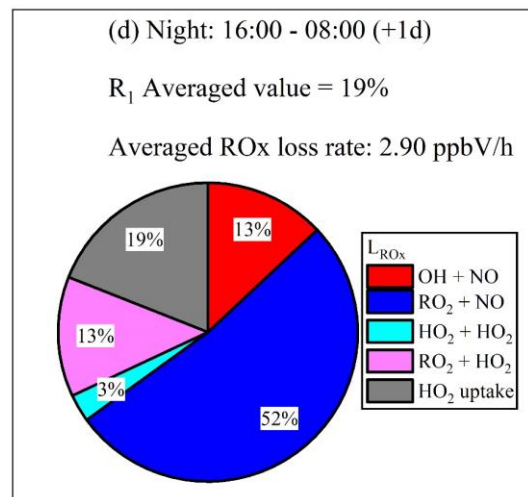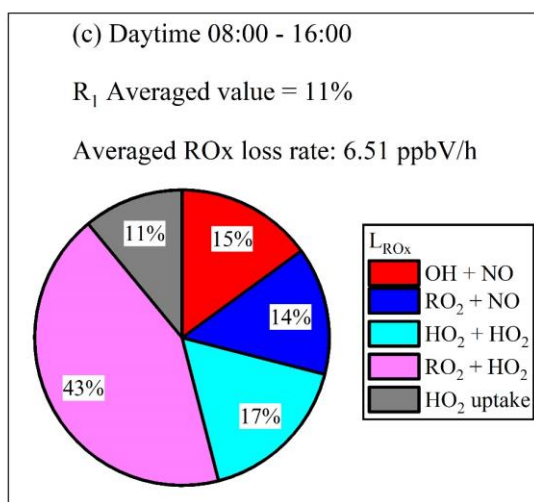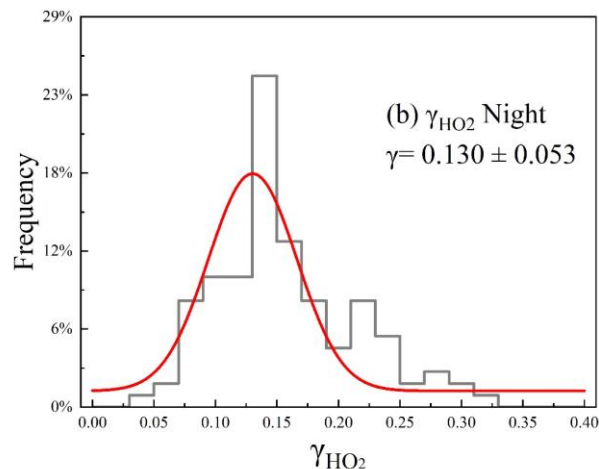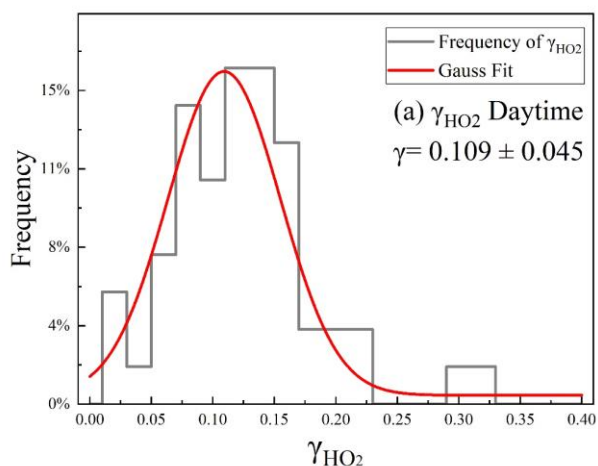[ASA] is the aerosol surface area [μm^2 cm^{-3}].

Figure 4: Daytime and night values of the HO_2 uptake coefficient (γ_{HO_2}) and R_1 calculated by the empirical equation (Equation 15). A Gaussian distribution (red line) is fitted to frequency distribution of γ_{HO_2} (a) and (b) yielding a mean uptake coefficient of 0.109 with a standard error of 0.045 in daytime and 0.130 with 0.053 at night. Pie charts show the values of R_1 and the loss rates for ROx during daytime (c) and nighttime (d). The averaged daytime (08:00−16:00) ROx radical loss rate is 6.5 ppbV/h and that for nighttime (16:00−08:00 (+1d)) is 2.9 ppbV/h.

In Fig. (These values are likely the maximum possible upper limit of γ_{HO_2} for near ground layer aerosols. Because of the distribution of TMI is mainly in the accumulation and coarse mode of aerosol, with the height increasing, the amount of copper in the aerosol decreases, leading to a decrease in the heterogeneous reaction rate of HO_2. The current empirical equation can only predict the maximum γ possible value of HO_2 heterogeneous uptake. When the aerosol mass concentration is constant, the gas phase resistance increases with the increasing of particle size, then the heterogeneous uptake coefficient of HO_2 is

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~~further reduced with larger particles. At the same time, the empirical equation can only estimate γ_{HO_2} at relative humidity of 40% to 90%, γ_{HO_2} is lower at the surface of dry aerosol. This further led to an overestimation of the HO₂ heterogeneous coefficient in this campaign.~~ 4 a and b), no significant difference of γ_{HO_2} is observed during daytime and night. The HO₂ uptake coefficient is slightly higher at night due to the higher *RH* (57.6% at day and 67.4% at night). HO₂ heterogeneous uptake reactions with aerosol particles have small impact on ROx radical termination at daytime as shown in Fig. (4 c). However, HO₂ uptake may be important in the termination of ROx radicals at night shown in Fig. (4 d). The daytime ratio R_1 is lower than it is at night because of the lack of photochemical reactions, thus a longer HO₂ lifetime at night. The high proportion of RO₂+NO during night is due to high [NO] at dawn.

The RO₂ concentration is also important when evaluating the impact of HO₂ uptake. Using the modeled value of RO₂ concentration in Wangdu campaign, a higher proportion of HO₂ uptake to about 21% of ROx sinks in daytime can be calculated. However, using the modified field measured RO₂ concentration in Wangdu campaign, HO₂ uptake is less important in the budget of ROx as shown in Fig (4 c), which is in line with the results from Tan et al. (2020).

4 Summary and conclusions

The impact of HO₂ aerosol uptake on the ROx budget is complicated by large uncertainties in the HO₂ uptake coefficient under ambient conditions. The novel empirical parameterisation is applicable under the assumption of steady-state concentrations and with metastable or liquid aerosol particles (if the ambient *RH* over a completely liquid aerosol decreases below the deliquescence *RH*, the aerosol may not crystalize immediately but may constitute a supersaturated aqueous solution (i.e., in the metastable state) (Song et al., 2018)). The approximate calculation of HO₂ concentration gradients within the aerosol particle condensed phase also cause deviations for larger particles. The bulk diffusion coefficient of HO₂ and other reactive molecules should be lower in the situation of semi-solid particles (Berkemeier et al., 2016;Shiraiwa et al., 2010;Mikhailov et al., 2009) and would change with the water activity and the organic components (Price et al., 2015). This aspect needs further studies. For crystalline or amorphous solid aerosol particles, HO₂ will undergo surface reactions and diffuse across the surface rather than be accommodated within the aerosol bulk. The MARK model has limitations in the calculation of γ_{HO_2} with semi-solid aerosol particles. In the Wangdu campaign, κ_{sca} (optical aerosol hygroscopicity parameter) ranges from 0.05 to 0.35 with an average of 0.22. The ambient *RH* during the Wangdu campaign shows significant diurnal variations and varies greatly from 15% to 97%, with an average value of 61% (Kuang et al., 2019) indicating that the percentage of solid aerosol particles is relatively low and hence do not significantly influence γ_{HO_2}.

The interaction between organics and soluble copper and the influence of organics on aerosol properties will lead to further uncertainty in the calculation of the uptake coefficient. Lakey et al~~.~~ (Lakey et al., 2016a;Lakey et al., 2015;Lakey et al., 2016b)

have also shown that the addition of ~~a~~an organic compound to ~~Cu(II)~~Cu^{2+} doped aerosols~~,~~ such as oxalic acid, which forms

oxalate ions $(C_2O_4)^{2-}$ in the aerosol, results in a lower value of γ_{HO_2} as such ions forms a complex with the TMI.

~~Taketaniet al. collected the filter samples of aerosol in Mts. Tai&Mang, North China(Taketani et al., 2012)~~Taketani et al. collected the filter samples of aerosol in Mts. Tai and Mts. Mang, North China (Taketani et al., 2012) and re-~~aerosolize~~aerosolized from the water extracts of sampled particles. The measured uptake coefficients for Mt. Tai samples ranged between 0.09 and 0.40, while those at Mt. Mang were between 0.13 and 0.34. ~~Because of the re-aerosol dissolution of particle filters by acid digestion, soluble copper and other TMI may higher than ambient aerosol particles, which may be the reason of overestimation of the HO₂ uptake coefficient. Li et. al~~Li et. al (Li et al., 2019b) ~~find~~suggest that the rapid decrease of PM$_{2.5}$ in China ~~will slow~~has slowed down the reactive uptake rate of HO$_2$ radicals by aerosol particles ~~may be a very important and pervasive factor~~and could have been themain reason for the increase in ozone in the North China Plain~~.~~ in the recent years. They ~~take γ_{HO_x} as~~apply a value of the uptake coeffient of of 0.2 in their model ~~calculation~~calculations. However, the results of the MARK model and of the empirical equation ~~calculations~~ in this paper suggest that the HO$_2$ uptake coefficient ~~is in general~~could be smaller and highly variable~~. Thus further~~ for typical conditions in the North China Plain. Further research is needed to study the effects of heterogeneous uptake of HO$_2$ on gas phase and heterogeneous ~~physicochemical~~physico-chemical reactions under different environmental conditions in different regions~~ and when the variability of γ_{HO_x} is considered...~~.
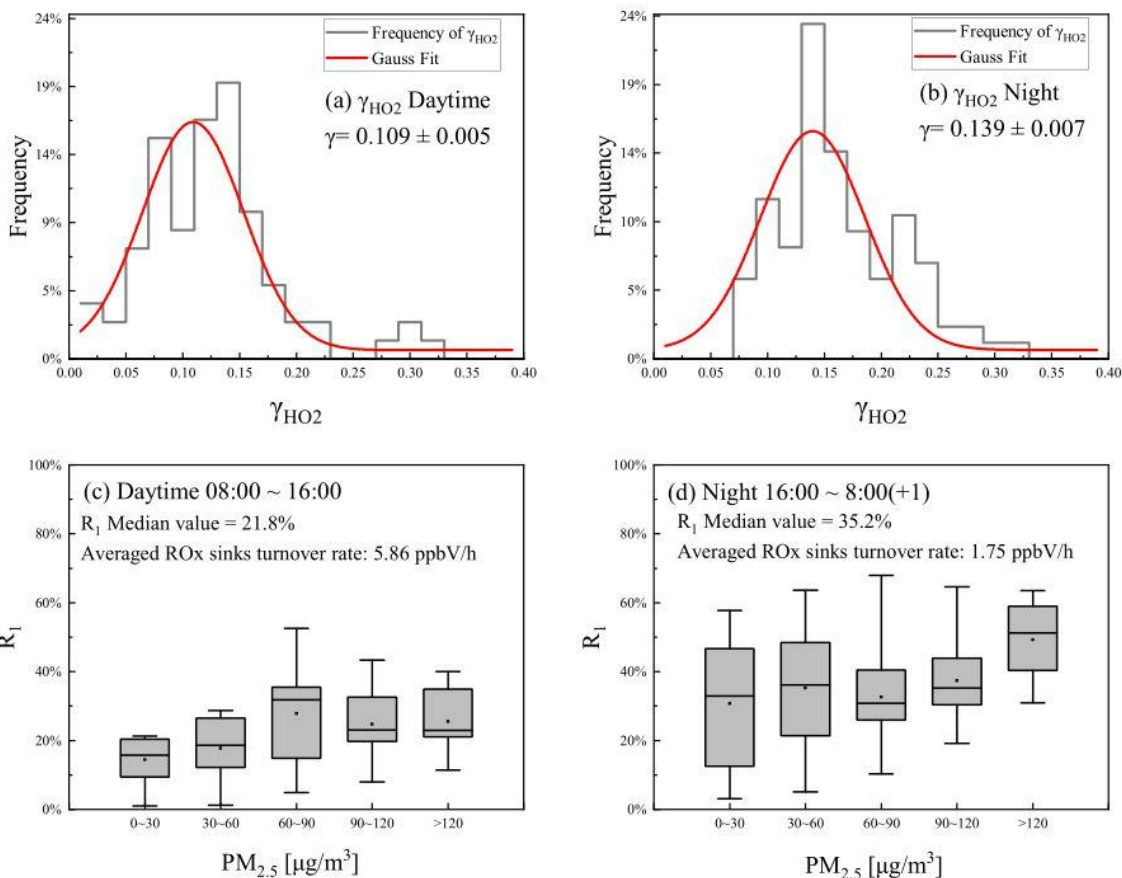
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Figure 6: Daytime and night γ_{HO_2} and R_1 calculated based on the new empirical equation. A Gaussian distribution (red line) is fitted to γ_{HO_2} frequency distribution in panel (a) and (b), yielding a mean uptake coefficient of 0.109 with a standard error of 0.005 in daytime and 0.139 with 0.007 at night. Box plot of R_1 according to aerosol mass concentration are shown in panel (c) and (d). No significant difference of R_1 in the whole range of aerosol mass loading may indicating that HO_2 uptake is

1280 equally important at different aerosol concentration. Daytime ratio is higher than it at night because of the low concentration of radicals hence the declines of ROx radical self reactions.

The experimental determined ROx termination rates include reaction channels from OH + NO$_2$ / NO, HO$_2$ + HO$_2$, HO$_2$ + RO$_2$, RO$_2$ + NO. Considering the solubility and size distribution of aerosol metal copper(Fang et al., 2017;Hsu et al.,

1285 2010a;Mao et al., 2013a) we can estimate γ_{HO_2} in daytime and night. Effective soluble Cu^{2+} used in the calculation is 25% of total aerosol metal copper concentration.

$$TR_{HO2uptake} = k_{uptake} \times [HO_2] \qquad (20)$$

$$R_1 = \frac{TR_{HO2uptake}}{TR_{HOxsinks}} \qquad (21)$$ The new parameterized equation proposed

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In Fig. (6), no significiant difference of γ_{HO_2} is observed during daytime and night. This shows that uptake process may be even more important on ROx budget with low radical concentration at night despite higher NOx concentration. The median values of R_1 in daytime and night have a small rise at relatively high aerosol concentration while having great uncertainties. Averaged daytime (08:00~16:00) ROx radical sinks turnover rate is 5.9 ppbV/h and that for nighttime (16:00~08:00(+1d)) is 1.7 ppbV/h.

3.4.5 The Uncertainty of the calculation in Wangdu campaign

Uncertainty of the calculation in this paper mainly come from the measurement of copper concentration, radical concentration and aerosol liquid water content. The combined standrad uncertainty (u_r) of the model calculations is a combination of uncertainties in the measurements used as model constraints and reaction rate constants. What's more, a series of tests based on Monte Carlo simulations show that the uncertainty of the model calculations is approximately 40% (for details, see Lu et al., 2012 and Tan et al., 2017)(Lu et al., 2012;Tan et al., 2017).

Table 7: Measured quantities used for data analysis and model calculations in Wangdu campaign

Measurement quantities	1σ Accuracy
Cu	±1.3%
Particle number size distribution (PNSD)	±2%
Relative humidity	±0.05%
Temperature	±0.05%
ALWC	±9.1 %
HO_2	±16%
RO_2	±18%
OH	±11%
NO	±20%

in this paper provides a novel way for more detailed calculation of the effects of HO_2 heterogeneous reactions on the atmospheric radical budget, ozone production and particulate matter generation. Overall, we can conclude that the HO_2 uptake process needs to be considered in photochemical box models for the study of the HOx radical budget. The exact value is highly variable with respect to the change of copper concentrations in the aerosol particle condensed phase and other factors. The measurement of condensed phase soluble copper and other TMIs, as well as the aerosol liquid water should be added for future field campaigns for the study of the HOx radical budget.

Author Contribution

Keding Lu conceived the study. Huan Song and Keding Lu developed the MARK model for multiphase simulations. Xiaorui Chen and Qi Zou improved the codes of the MARK model. Zhaofeng Tan, Hendrik Fuchs, Keding Lu, Alfred Wiedensohler, Mei Zheng, Andreas Wahner, Astrid Kiendler-Scharr, Yuanhang Zhang contributed to the related measurements of the Wangdu field campaign. Dwayne E. Heard, Daniel R. Moon and Maríá-Teresa Baeza-Romero contributed the laboratory studies of HO_2 uptake coefficients and they have contributed to writing the manuscript. Huan Song performed the model simulations and prepared the manuscript with Keding Lu and Zhaofeng Tan which was enhanced by contributions from all the co-authors.

Competing Interest

The authors have no conflict of interests.

Data Availability

Data supporting this publication are avaiable upon request for the corresponding author (k.lu@pku.edu.cn).

~~. The reaction rates of Fe/Mn for liquid phase HO_2 in aerosol is about 100 times slower than it is for Cu. The influence of aerosol Fe and Mn on HO_2 uptake can be neglected compared to Cu or scaled as equivalent $[Cu^{2+}]$ according to the difference of their rate constants with HO_2. Overall, we can conclude that the HO_2 uptake process needs to be considered in the photochemical box model for the study of the HOx radical budget. The exact value is highly variable with respect to the change of copper concentrations in the aerosol liquid water. The measurement of soluble copper and other TMIs as well as the aerosol liquid water shall be added for future field campaign for the study of HOx radical budget.~~

References

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI - heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, 10.5194/acp-13-8045-2013, 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.

1335   Baker, A. R., and Jickells, T. D.: Mineral particle size as a control on aerosol iron solubility, Geophysical Research Letters, 33, 10.1029/2006gl026557, 2006.

Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Pöschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy, semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, Physical Chemistry Chemical Physics, 18, 12662-12674, 2016.

1340   Bian, Y. X., Zhao, C. S., Ma, N., Chen, J., and Xu, W. Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, Atmos. Chem. Phys., 14, 6417-6426, 10.5194/acp-14-6417-2014, 2014.

Bielski, B. H., Cabelli, D. E., Arudi, R. L., and Ross, A. B.: Reactivity of HO_2/O_2^- radicals in aqueous solution, Journal of physical and chemical reference data, 14, 1041-1100, 1985.

Capps, S., Henze, D., Hakami, A., Russell, A., and Nenes, A.: ANISORROPIA: the adjoint of the aerosol thermodynamic model

1345   ISORROPIA, Atmospheric Chemistry & Physics, 12, 2012.

Chameides, W. L., and Stelson, A. W.: Aqueous-phase chemical processes in deliquescent seasalt aerosols, Ber Bunsen Phys Chem, 96, 461-470, 1992.

Cheng, M. C., You, C. F., Cao, J. J., and Jin, Z. D.: Spatial and seasonal variability of water-soluble ions in PM2.5 aerosols in 14 major cities in China, Atmos. Environ., 60, 182-192, 10.1016/j.atmosenv.2012.06.037, 2012.

1350   Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures, Journal of Physical Chemistry A, 102, 2137-2154, 10.1021/jp973042r, 1998.

Cooper, P. L., and Abbatt, J. P. D.: Heterogeneous interactions of OH and HO_2 radicals with surfaces characteristic of atmospheric particulate matter, J Phys Chem-Us, 100, 2249-2254, Doi 10.1021/Jp952142z, 1996.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939-

1355   7954, 10.5194/acp-19-7939-2019, 2019.

Ervens, B., George, C., Williams, J. E., Buxton, G. V., Salmon, G. A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, J. Geophys. Res.-Atmos., 108, 10.1029/2002jd002202, 2003.

Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative

1360   Potential: A Link between Sulfate and Aerosol Toxicity, Environ. Sci. Technol., 51, 2611-2620, 10.1021/acs.est.6b06151, 2017.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-$Nh(4)(+)$ NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--$H2O$ aerosols, Atmos. Chem. Phys., 7, 4639-4659, 2007.

George, I. J., Matthews, P. S. J., Whalley, L. K., Brooks, B., Goddard, A., Baeza-Romero, M. T., and Heard, D. E.: Measurements of uptake coefficients for heterogeneous loss of HO2 onto submicron inorganic salt aerosols, Physical Chemistry Chemical Physics, 15, 12829-12845,

1365   10.1039/c3cp51831k, 2013.

Goliff, W. S., and Stockwell, W. R.: The regional atmospheric chemistry mechanism, version 2, an update, International con-ference on Atmospheric Chemical Mechanisms, University of California, Davis, 96, 36, 2008.

Goliff, W. S., Stockwell, W. R., and Lawson, C. V.: The regional atmospheric chemistry mechanism, version 2, Atmos. Environ., 68, 174-185, 2013.

1370   Golden, D. M., Bierbaum, V. M., and Howard, C. J.: Re-evaluation of the bond-dissociation energies (Delta-Hdbe) for H-OH, H-OOH, H-OO-, H-O., H-OO-, and H-OO, J Phys Chem-Us, 94, 5413-5415, 10.1021/j100376a046, 1990.

Graedel, T., and Weschler, C.: Chemistry within aqueous atmospheric aerosols and raindrops, Reviews of Geophysics, 19, 505-539, 1981.

Graedel, T. E., Mandich, M. L., and Weschler, C. J.: KINETIC MODEL STUDIES OF ATMOSPHERIC DROPLET CHEMISTRY .2. HOMOGENEOUS TRANSITION-METAL CHEMISTRY IN RAINDROPS, J.: Kinetic-model studies of atmospheric droplet chemistry.

1375   2. Homogeneous transition-metal chemistry in raindrops, J. Geophys. Res.-Atmos., 91, 5205-5221, 10.1029/JD091iD04p05205, 1986.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci Rep-Uk, 7, 12109, 10.1038/s41598-017-11704-0, 2017.

Hanson, D. R., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of OH and HO_2 radical uptake coefficients on water and sulfuric-acid surfaces, J Phys Chem-Us, 96, 4979-4985, Doi 10.1021/J100191a046, 1992.

1380   Hanson, D. R., Ravishankara, A. R., and Solomon, S.: HETEROGENEOUS REACTIONS IN SULFURIC ACID AEROSOLS - A FRAMEWORK FOR MODEL CALCULATIONS, J.: Heterogeneous reactions in sulfuric-acid aerosol: A framework for model calculations, J. Geophys. Res.-Atmos., 99, 3615-3629, 10.1029/93jd02932, 1994.

Hsu, S.-C., Wong, G. T. F., Gong, G.-C., Shiah, F.-K., Huang, Y.-T., Kao, S.-J., Tsai, F., Candice Lung, S.-C., Lin, F.-J., Lin, I. I., Hung, C.-C., and Tseng, C.-M.: Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea, Marine Chemistry, 120,

1385   116-127, https://doi.org/10.1016/j.marchem.2008.10.003, 2010a.

Hsu, S. C., Liu, S. C., Lin, C. Y., Hsu, R. T., Huang, Y. T., and Chen, Y. W.: Metal compositions of PM_{10} and $PM_{2.5}$ aerosols in Taipei during spring, 2002, Terrestrial Atmospheric and Oceanic Sciences, 15, 925-948, 10.3319/tao.2004.15.5.925(adse), 2004.

Hsu, S. C., Liu, S. C., Tsai, F., Engling, G., Lin, II, Chou, C. K. C., Kao, S. J., Lung, S. C. C., Chan, C. Y., Lin, S. C., Huang, J. C., Chi, K. H., Chen, W. N., Lin, F. J., Huang, C. H., Kuo, C. L., Wu, T. C., and Huang, Y. T.: High wintertime particulate matter pollution over an

1390   offshore island (Kinmen) off southeastern China: An overview, J. Geophys. Res.-Atmos., 115, 10.1029/2009jd013641, 2010b.

Huie, R. E.: NDRL/NIST Solution Kinetics Database on the WEB, Journal of Research (NIST JRES)-, 108, 2003.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmos. Environ., 34, 2131-2159, 10.1016/s1352-2310(99)00462-8, 2000.

Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Tanimoto, H., Kato, S., Suthawaree, J., Inomata, S., Taketani, F., Okuzawa, K., Kawamura, K., Akimoto, H., and Wang, Z. F.: Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors, Atmos. Chem. Phys., 9, 7711-7723, 2009.

Khvorostyanov, V. I., and Curry, J. A.: Refinements to the Köhler's theory of aerosol equilibrium radii, size spectra, and droplet activation: Effects of humidity and insoluble fraction, Journal of Geophysical Research: Atmospheres, 112, 2007.

Kolb, C., Worsnop, D., Zahniser, M., Davidovits, P., Keyser, L., Leu, M.-T., Molina, M., Hanson, D., Ravishankara, A., and Williams, L.: Laboratory studies of atmospheric heterogeneous chemistry, in: Progress and problems in atmospheric chemistry, World Scientific, 771-875, 1995.

Kuang, Y., Zhao, C. S., Zhao, G., Tao, J. C., Xu, W. Y., Ma, N., and Bian, Y. X.: A novel method for calculating ambient aerosol liquid water content based on measurements of a humidified nephelometer system, Atmos Meas Tech, 11, 2967-2982, 10.5194/amt-11-2967-2018, 2018.

Kuang, Y., Tao, J., Xu, W., Yu, Y., Zhao, G., Shen, C., Bian, Y., and Zhao, C.: Calculating ambient aerosol surface area concentrations using aerosol light scattering enhancement measurements, Atmos. Environ., 216, 116919, https://doi.org/10.1016/j.atmosenv.2019.116919, 2019.

Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO_2 Uptake Coefficients onto Single Component Organic Aerosols, Environ. Sci. Technol., 49, 4878-4885, 10.1021/acs.est.5b00948, 2015.

Lakey, P. S. J., Berkemeier, T., Krapf, M., Dommen, J., Steimer, S. S., Whalley, L. K., Ingham, T., Baeza-Romero, M. T., Pöschl, U., Shiraiwa, M., Ammann, M., and Heard, D. E.: The effect of viscosity on the ~~HO₂~~HO_2 uptake by sucrose and secondary organic aerosol particles, Atmospheric Chemistry and Physics Discussions, 1-25, 10.5194/acp-2016-284, 2016a.

Lakey, P. S. J., George, I. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Organics Substantially Reduce HO_2 Uptake onto Aerosols Containing Transition Metal ions, Journal of Physical Chemistry A, 120, 1421-1430, 10.1021/acs.jpca.5b06316, 2016b.

Lelieveld, J., and Crutzen, P. J.: The role of clouds in tropospheric photochemistry, J Atmos Chem, 12, 229-267, 10.1007/bf00048075, 1991.

Lewis, J., Argyle, R., Bunclarck, P., Evans, D., Gonzales-Solares, E., and Markwardt, C. B.: Non-linear Least Squares Fitting in IDL with MPFIT, arXiv preprint arXiv:0902.2850, 2009.

Li, H., Wang, D., Cui, L., Gao, Y., Huo, J., Wang, X., Zhang, Z., Tan, Y., Huang, Y., Cao, J., Chow, J. C., Lee, S.-c., and Fu, Q.: Characteristics of atmospheric PM2.5 composition during the implementation of stringent pollution control measures in shanghai for the 2016 G20 summit, Sci. Total Environ., 648, 1121-1129, 10.1016/j.scitotenv.2018.08.219, 2019a.

Li, K., Jacob, D. J., Liao, H., Shen, L., Zhang, Q., and Bates, K. H.: Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, Proceedings of the National Academy of Sciences, 116, 422, 10.1073/pnas.1812168116, 2019b.

Lou, S., Liao, H., and Zhu, B.: Impacts of aerosols on surface-layer ozone concentrations in China through heterogeneous reactions and changes in photolysis rates, Atmos. Environ., 85, 123-138, 10.1016/j.atmosenv.2013.12.004, 2014.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Haseler, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO2 concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, Atmos. Chem. Phys., 12, 1541-1569, 10.5194/acp-12-1541-2012, 2012.

Lundström, T., Christensen, H., and Sehested, K.: Reactions of the HO2 radical with OH, H, Fe2+ and Cu2+ at elevated temperatures, Radiation Physics and Chemistry, 69, 211-216, 2004.

Macintyre, H., and Evans, M.: Parameterisation and impact of aerosol uptake of ~~HO 2~~HO_2 on a global tropospheric model, Atmos. Chem. Phys., 11, 10965-10974, 2011.

Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., St Clair, J. M., Crounse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaegle, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HOx) in the Arctic troposphere in spring, Atmos. Chem. Phys., 10, 5823-5838, 10.5194/acp-10-5823-2010, 2010.

Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, Atmos. Chem. Phys., 13, 509-519, 10.5194/acp-13-509-2013, 2013a.

Mao, J. Q., Paulot, F., Jacob, D. J., Cohen, R. C., Crounse, J. D., Wennberg, P. O., Keller, C. A., Hudman, R. C., Barkley, M. P., and Horowitz, L. W.: Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res.-Atmos., 118, 11256-11268, 10.1002/jgrd.50817, 2013b.

Markwardt, C. B.: Non-linear least squares fitting in IDL with MPFIT, arXiv preprint arXiv:0902.2850, 2009.

Martin, R. V., Jacob, D. J., Yantosca, R. M., Chin, M., and Ginoux, P.: Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, J. Geophys. Res.-Atmos., 108, Artn 4097
10.1029/2002jd002622, 2003.

Martinez, M., Harder, H., Kovacs, T. A., Simpas, J. B., Bassis, J., Lesher, R., Brune, W. H., Frost, G. J., Williams, E. J., Stroud, C. A., Jobson, B. T., Roberts, J. M., Hall, S. R., Shetter, R. E., Wert, B., Fried, A., Alicke, B., Stutz, J., Young, V. L., White, A. B., and Zamora,

R. J.: OH and HO_2 concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999, J. Geophys. Res.-Atmos., 108, Artn 4617 10.1029/2003jd003551, 2003.

1450 Matthews, P. S. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Uptake of HO_2 radicals onto Arizona test dust particles using an aerosol flow tube, Atmos. Chem. Phys., 14, 7397-7408, 10.5194/acp-14-7397-2014, 2014.

~~Moon, D. R., Taverna, G.~~Mikhailov, E., Vlasenko, S., ~~Anduix-Canto, C., Ingham,~~Martin, S. T., ~~Chipperfield, M. P., Seakins, P. W., Baeza-Romero, M.~~Koop, T., and ~~Heard, D. E.: Heterogeneous reaction of HO2 with airborne TiO2~~Poschl, U.: Amorphous and crystalline aerosol

1455 particles ~~and its implication~~interacting with water vapor: conceptual framework and experimental evidence for ~~climate change mitigation strategies~~restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., ~~18, 327-338, 10.5194/acp-18-327-2018, 2018~~9, 9491-9522, 2009.

Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G.~~: MASS ACCOMMODATION COEFFICIENT FOR HO2 RADICALS ON AQUEOUS PARTICLES~~: Mass accommodation coefficient for HO_2 radicals on aqueous particles, J. Geophys. Res.-Atmos., 92, 4163-4170, 10.1029/JD092iD04p04163, 1987.

1460 Oakes, M., Weber, R., Lai, B., Russell, A., and Ingall, E.: Characterization of iron speciation in urban and rural single particles using XANES spectroscopy and micro X-ray fluorescence measurements: investigating the relationship between speciation and fractional iron solubility, Atmos. Chem. Phys., 12, 745, 2012.

Price, H. C., Mattsson, J., Zhang, Y., Bertram, A. K., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., and Rickards, A. M.: Water diffusion in atmospherically relevant α-pinene secondary organic material, Chem Sci, 6, 4876-4883, 2015.

1465 Ross, H. B., and Noone, K. J.~~: A NUMERICAL INVESTIGATION OF THE DESTRUCTION OF PEROXY RADICAL BY CU ION CATALYZED REACTIONS ON ATMOSPHERIC PARTICLES~~: A numerical investigation of the destruction of peroxy radical by Cu ion catalyzed-reactions of atmospheric particles, J Atmos Chem, 12, 121-136, 10.1007/bf00115775, 1991.

~~Schwartz, S. A., and Meyer, G. A.: CHARACTERIZATION OF AEROSOLS GENERATED BY THERMOSPRAY NEBULIZATION FOR ATOMIC SPECTROSCOPY, Spectrochimica Acta Part B-Atomic Spectroscopy, 41, 1287-1298, 10.1016/0584-8547(86)80007-6,~~

1470 ~~1986.~~

Sander, R.: Modeling atmospheric chemistry: Interactions between gas-phase species and liquid cloud/aerosol particles, Surveys in Geophysics, 20, 1-31, 1999.

Schwartz, S. E., and Freiberg, J. E.~~: MASS TRANSPORT LIMITATION TO THE RATE OF REACTION OF GASES IN LIQUID DROPLETS - APPLICATION TO OXIDATION OF~~: Mass-transport limitation of the rate of reaction of gases in liquid droplets-application

1475 to oxidation of SO_2 ~~IN AQUEOUS SOLUTIONS~~in aqueous solutions, Atmos. Environ., 15, 1129-1144, 10.1016/0004-6981(81)90303-6, 1981.

Schwartz, S. E.~~: GAS-PHASE AND AQUEOUS PHASE CHEMISTRY OF~~: Gas phase and aqueous phase chemistry of HO_2 ~~IN LIQUID WATER CLOUDS~~in liquid water clouds, J. Geophys. Res.-Atmos., 89, 1589-1598, 10.1029/JD089iD07p11589, 1984.

Schwartz, S. E.~~: BOTH SIDES NOW - THE CHEMISTRY OF CLOUDS~~: Mass-transport considerations pertinent to aqueous phase

1480 reactions of gases in liquid-water clouds, in: Chemistry of multiphase atmospheric systems, Springer, 415-471, 1986.

Schwartz, S. E.: Both sides now-The chemistry of clouds, Annals of the New York Academy of Sciences, 502, 83-144, 10.1111/j.1749-6632.1987.tb37648.x, 1987.

Seinfeld, J. H.: ES&T books: atmospheric chemistry and physics of air pollution, Environ. Sci. Technol., 20, 863-863, 1986.

Shiraiwa, M., Pfrang, C., and Poschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of

1485 interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, Atmos. Chem. Phys., 10, 3673-3691, 10.5194/acp-10-3673-2010, 2010.

Song, S. J., Gao, M., Xu, W. Q., Shao, J. Y., Shi, G. L., Wang, S. X., Wang, Y. X., Sun, Y. L., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

1490 Taketani, F., Kanaya, Y., and Akimoto, H.~~: Kinetics of heterogeneous reactions of HO2 radical at ambient concentration levels with (NH4)(2)SO4 and NaCl aerosol particles, Journal of Physical Chemistry A, 112, 2370-2377, 10.1021/jp0769936, 2008a.~~

~~Taketani, F., Kanaya, Y., and Akimoto, H.~~: Kinetics of heterogeneous reactions of HO_2 radical at ambient concentration levels with $(NH_4)_2SO_4$ and NaCl aerosol particles, The Journal of Physical Chemistry A, 112, 2370-2377, ~~2008b~~2008.

Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous loss of HO_2 by KCl, synthetic sea salt, and natural seawater aerosol particles,

1495 Atmos. Environ., 43, 1660-1665, 2009.

Taketani, F., and Kanaya, Y.: Kinetics of HO_2 Uptake in Levoglucosan and Polystyrene Latex Particles, J Phys Chem Lett, 1, 1701-1704, 10.1021/jz100478s, 2010.

Taketani, F., Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Okuzawa, K., Kawamura, K., Wang, Z., and Akimoto, H.: Measurement of overall uptake coefficients for HO_2 radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang (China), Atmos. Chem. Phys., 12,

1500 11907-11916, 10.5194/acp-12-11907-2012, 2012.

Tan, Z., Hofzumahaus, A., Lu, K., Brown, S. S., Holland, F., Huey, L. G., Kiendler-Scharr, A., Li, X., Liu, X., and Ma, N.: No Evidence for a Significant Impact of Heterogeneous Chemistry on Radical Concentrations in the North China Plain in Summer 2014, Environ. Sci. Technol., 2020.

Tan, Z. F., Fuchs, H., Lu, K. D., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H. B., Gomm, S., Haseler, R., He, L. Y., Holland, F., Li, X., Liu, Y., Lu, S. H., Rohrer, F., Shao, M., Wang, B. L., Wang, M., Wu, Y. S., Zeng, L. M., Zhang, Y. S., Wahner, A., and Zhang, Y. H.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO$_2$ and RO$_2$ radicals, Atmos. Chem. Phys., 17, 663-690, 10.5194/acp-17-663-2017, 2017.

Tang, M. J., Huang, X., Lu, K. D., Ge, M. F., Li, Y. J., Cheng, P., Zhu, T., Ding, A. J., Zhang, Y. H., Gligorovski, S., Song, W., Ding, X., Bi, X. H., and Wang, X. M.: Heterogeneous reactions of mineral dust aerosol: implications for tropospheric oxidation capacity, Atmos. Chem. Phys., 17, 11727-11777, 10.5194/acp-17-11727-2017, 2017.

Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning PM 2. PM$_{2.5}$ chemical composition, aerosol optical properties and their relationships across China, Atmos. Chem. Phys., 17, 9485, 2017.

Thornton, J., and Abbatt, J. P. D.: Measurements of HO$_2$ uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, Journal of Geophysical Research: Atmospheres, J. Geophys. Res.-Atmos., 110, n/a-n/a, 10.1029/2004JD0054022004jd005402, 2005.

Thornton, J. A., Jaegle, L., and McNeill, V. F.: Assessing known pathways for HO$_2$ loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, Journal of Geophysical Research: Atmospheres, 113, 2008.

Tie, X., Brasseur, G., Emmons, L., Horowitz, L., and Kinnison, D.: Effects of aerosols on tropospheric oxidants: A global model study, J. Geophys. Res.-Atmos., 106, 22931-22964, Doi 10.1029/2001jd900206, 2001.

Vlasenko, S. S., Su, H., Pöschl, U., Andreae, M. O., and Mikhailov, E. F.: Tandem configuration of differential mobility and centrifugal particle mass analysers for investigating aerosol hygroscopic properties, Atmos Meas Tech, 10, 1269, 2017.

Whalley, L. K., Furneaux, K. L., Goddard, A., Lee, J. D., Mahajan, A., Oetjen, H., Read, K. A., Kaaden, N., Carpenter, L. J., Lewis, A. C., Plane, J. M. C., Saltzman, E. S., Wiedensohler, A., and Heard, D. E.: The chemistry of OH and HO$_2$ radicals in the boundary layer over the tropical Atlantic Ocean, Atmos. Chem. Phys., 10, 1555-1576, 10.5194/acp-10-1555-2010, 2010.

Whalley, L. K., Stone, D., George, I. J., Mertes, S., van Pinxteren, D., Tilgner, A., Herrmann, H., Evans, M. J., and Heard, D. E.: The influence of clouds on radical concentrations: observations and modelling studies of HOx during the Hill Cap Cloud Thuringia (HCCT) campaign in 2010, Atmos. Chem. Phys., 15, 3289-3301, 10.5194/acp-15-3289-2015, 2015.

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, Atmos. Chem. Phys., 14, 13175-13188, 10.5194/acp-14-13175-2014, 2014.

Yin, J., Allen, A. G., Harrison, R. M., Jennings, S. G., Wright, E., Fitzpatrick, M., Healy, T., Barry, E., Ceburnis, D., and McCusker, D.: Major component composition of urban PM10 and PM2.5 in Ireland, Atmos. Res., 78, 149-165, https://doi.org/10.1016/j.atmosres.2005.03.006, 2005.

Zhou, J., Murano, K., Kohno, N., Sakamoto, Y., and Kajii, Y.: Real-time quantification of the total HO$_2$ reactivity of ambient air and HO$_2$ uptake kinetics onto ambient aerosols in Kyoto (Japan), Atmos. Environ., 223, 117189, https://doi.org/10.1016/j.atmosenv.2019.117189, 2020.

Zou, Q., Song, H., Tang, M., and Lu, K.: Measurements of HO$_2$ uptake coefficient on aqueous (NH$_4$)$_2$SO$_4$ aerosol using aerosol flow tube with LIF system, Chinese Chemical Letters, https://doi.org/10.1016/j.cclet.2019.07.041, 2019.