Response to the comments of reviewer #3:

Comment:

This paper describes a new parameterization for the reaction probability of HO2 on Cu-containing aerosol particles. The reactive uptake of HO2 to aerosol remains an uncertain but potentially important component of atmospheric HOx fate, and has gained renewed attention of late. There is thus a reasonable need for more evaluation of how HO2 reactive uptake is described in models and this paper therefore has scientific merit and is appropriate in scope for ACP. We thank the reviewer for the 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 in order to avoid the confusion between the two parameterized equations mentioned in the MS, the classical parameterization equation (proposed by IUPAC) is abbreviated as *CEq.*, and the parameterization proposed in this paper is abbreviated as *NEq.*. We have added these two abbreviations to make the language more concise in the revised MS.

Comment:

However, I have several concerns about the scientific quality and presentation in the manuscript that I think should be addressed before the paper is published. I describe these concerns below.

1) Uncertainty - overview. There is little objective discussions of measurement uncertainty and about uncertainties regarding application of the parameterization.

For the new experimental dataset included in the paper, the final uncertainty in the uptake coefficient is calculated via the propagation of errors. The uncertainty of the averaged HO_2 signal is calculated as 1σ of the average of the data points recorded during the averaging period (20 s). The pseudo first-order loss rate coefficient (k') was obtained from the gradient of a plot of ln(HO_2 signal) against reaction time, the error for k' was 1σ of the uncertainty of the gradient and was obtained from the plotting software, Origin Pro (v.9.0). The uptake coefficient ($\gamma(HO_2)$) was obtained from the gradient of the plot of k' against the surface area concentration of aerosols in the flow tube. The error given on all measurements of $\gamma(HO_2)$ represents 2σ of the uncertainty of the gradient also calculated in Origin Pro. For all calculations, errors were propagated using the standard laws of error propagation. The Brown correction calculation, used to correct k' for non-plug flow conditions in the flow tube, is complex and is performed by a FORTRAN subroutine called ROOT. When propagating error through Brown correction calculations the correction factor was determined by plotting the Brown corrected pseudo-first-order rate constant, k´, against the uncorrected observed rate constant minus the rate constant observed during the wall loss run resulting in a linear plot. The gradient of such a plot was the correction factor calculated by ROOT and was also applied to the uncertainty of k'. See further discussion about uncertainties in the new experimental dataset in the response to the next referee´s comment.

This is only for the Leeds data, and does not necessarily apply to other experimental data from other groups. Although the MARK model simulation results in this paper are not obtained by adjusting parameters to fit the experimental data points, laboratory measurement uncertainties will directly influence the evaluation of the deviation between the modelled HO_2 uptake coefficient and the measured results because all the parameters inputted in the MARK model are in reference to the measurement conditions. However, it is difficult to calculate the detailed uncertainties from all factors that influence γ_{HO_2} because of the nonlinear reaction system. What is more, uncertainties of the experimental conditions such as RH and particle diameters are combined into the reported values of γ_{HO_2}. Taking all these into account, we calculated an averaged uncertainty for the experimental values of γ_{HO_2} in different ranges of Cu ions concentration.

1.1There is apparently a new data set on measured gamma_HO2, but there is *very little* discussion of those measurements, how they were made, how the uncertainty was determined etc. The relative uncertainty for the new data at high Cu is nearly an order of magnitude lower than that reported for other measurements in the literature.

We agree with the referee that there is little discussion on the new measurements, the reason being that additional authors for these new measurements were added to the paper at the revised stage, and the original paper had no description of the experimental method. We have now included a brief description of the experimental set up used for these measurements.

With regards to the new measurements reported in this paper, the reason for the decrease in measurement uncertainty compared with our previous measurements, was a series of improvements developed in the experimental methodology that allow a better signal to noise ratio and more reproducible results to be obtained. For example, the sensitivity towards HO_2, quantified by calibration, was typically an order of magnitude better for these experiments, resulting in significantly smaller measurement error bars at each point along the flow tube. The improved uncertainty on each data point resulted in a higher quality decay of the HO_2 signal down the flow tube and a better linear fit of the plot of the natural log of the HO_2 FAGE signal versus contact time, resulting in a lower degree of uncertainty on the fit and hence the derived pseudo first order rate constant, k’, from it. Methodology included increasing the degree of averaging, allowing longer times for the stepper-motor to stabilize the sliding injector for each of its positions in the flow tube, more frequent cleaning of the atomizer, cleaning the set up with deionized water between different experiments, the use of longer times for the aerosol concentration to stabilize between experiments. In addition, the aerosol flow tube was cleaned on a weekly basis with distilled water and a new coating of halocarbon wax applied for each new aerosol system investigated. It was observed that this in-depth cleaning and longer stabilization times between experiments (e.g. performed with different Cu concentrations) led to highly reproducible results which translated into significantly reduced uncertainties in the uptake coefficients. All these factors promote a reduction in the uncertainties of our measurements.

The reason for the large uncertainties for Thornton et al. and Taketani et al. at the highest Cu concentrations is not clear. For the Thornton et al. dataset this could be related to the use of a completely different set up for the detection of HO_2 radicals which is less sensitive than FAGE. For the Taketani et al. dataset who used a very similar FAGE set up, it could be related to some of the factors listed above related to the experimental procedure. Moreover, for the Taketani et al. dataset, the quoted errors are given for two standard deviations from the least-squares fits (95% confidence limits), which is then combined with the estimated systematic uncertainties in the measurements of aerosol surface concentration (5%) and flow speed (2%). Our quoted uncertainties did not include any systematic uncertainties in our measurements as they are small compared to the random, statistical error.

In the revised MS, we have added the following text related to the experimental set up in Section 2.3 in the revised MS:

"The experimental setup and methodology used to make the new measurements of $\gamma(HO_2)$ reported here have been described in detail elsewhere (Moon et al., 2018b; Lakey et al., 2016c; George et al., 2013) and so only brief details are given here. In summary, the experiments were performed by moving an HO_2 injector backwards and forwards along the concentric axis of a laminar aerosol flow tube hence changing the contact time between HO_2 and the aerosols. Measurements of $[HO_2]$ were performed using laser induced fluorescence (LIF) spectroscopy at low-pressure (the fluorescence assay by gas expansion (FAGE) technique (Heard and Pilling, 2003)) and the total aerosol surface area was determined with a Size Mobility Particle Sizer (SMPS) at the end of the flow tube. Aerosols were formed using a constant output atomiser (TSI, 3076) and the aerosol concentration and hence surface area could be varied, being controlled using a high efficiency particulate air (HEPA) filter in a bypass arrangement. Atomiser solutions were prepared by dissolving 0.01 moles of ammonium sulphate (AS) (Fisher scientific, >99%) with varying amounts of copper (II) sulphate (Fisher scientific, >98%) in 500 mL of Milli-Q water. The data were analysed as described in George et al 2013. The pseudo first-order loss rate coefficient (k') was obtained from the gradient of a plot of ln(HO_2 signal) against the interaction time between HO_2 and the aerosol before sampling by the FAGE detector. The uptake coefficient ($\gamma(HO_2)$) was obtained from the linear least-squares gradient of the plot of k' against the surface area concentration of aerosols in the flow tube. The error given on all measurements of $\gamma(HO_2)$ represents 2σ of the uncertainty of the fitted gradient. A correction to k' was applied to taking into account non-plug flow conditions in the flow tube using the Brown method."

Comment:

Given that the parameterization is developed by comparing a mechanistic model to multiple data sets from different experiments - how each data point is weighted and the role of the relative uncertainty needs to be discussed. Best would be to show some portion of the raw data from the new measurements and step through how the uncertainty propagates to the reported gamma_HO2.

We changed the Section 3.2 in the MS and discuss the uncertainties influence in the revised MS:

"What is more, laboratory measurement uncertainties will directly influence the evaluation of the deviation between the modelled HO_2 uptake coefficient and the measured results because all the parameters inputted in the MARK model are in reference to the measurement conditions. However, it is difficult to calculate the detailed uncertainties from all factors that influence γ_{HO_2} because of the nonlinear reaction system. Uncertainties of the experimental conditions such as RH and particle diameters are combined into the reported values of γ_{HO_2}. Taking all these into account, we calculated an averaged uncertainty for the experimental values of γ_{HO_2} in different ranges of Cu ions concentration. Laboratory measurement uncertainty has the largest value of 35.1% in the range of 1×10^{-4} to 0.01 M soluble copper concentration, 14.9% below 1×10^{-4} M and 9.3% higher than 0.01 M."

We used the weighted average values of each datapoint uncertainty when calculating RMSE as the following equation. RMSE is now changed to 0.13 considering the relative uncertainty of measured data.

We add the following statement in section 3.2 in the revised MS:

"In this paper, the relative error of each measured data point is considered to calculate the weighted average in RMSE:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}((log_{10}^{u_{i_{measured}}} - log_{10}^{u_{i_{model}}})^{2}(\omega_i)^2)}{\sum_{i=1}^{n}(\omega_i)^2 \cdot n}}$$

$u_{i_{model}}$ is the MARK model result at each Cu^{2+} concentration and RH, $u_{i_{measured}}$ is the central value of each measurement result and ω_i is its corresponding relative error."

Comment:

1.2 It seems to me that little can be concluded about the effects of RH given the spread of measurement values at the same RH. While the model has a RH dependence built in through activity coefficients and Cu concentrations, etc, there is no real comparison of the modeled predicted RH dependence with the measurements where a plot of gamma_HO2 for a given Cu mass fraction would be shown versus RH.

The MARK model simulation results in this paper are not obtained by adjusting parameters to fit the experimental data points. At present, there are experimental measurements of γ_{HO_2} at different RH but there is no experimental systematic study of this dependence where only RH is changed and no other parameters. Many researches proposed that γ_{HO_2} is higher for aqueous inorganic aerosol than for dry inorganic aerosol. Although the previous experiments did not directly measure the RH´s dependence, the change of the experimental uptake coefficients met the simulation trend (see Figure 2). Ambient RH would affect 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. The MARK model was presented to simulate the change of the uptake coefficient with RH in Figure 1. Moreover, we also did simulations in the MARK model of HO_2 uptake with dilute solution droplets with no consideration of RH and update the Figure 2 in the revised MS.

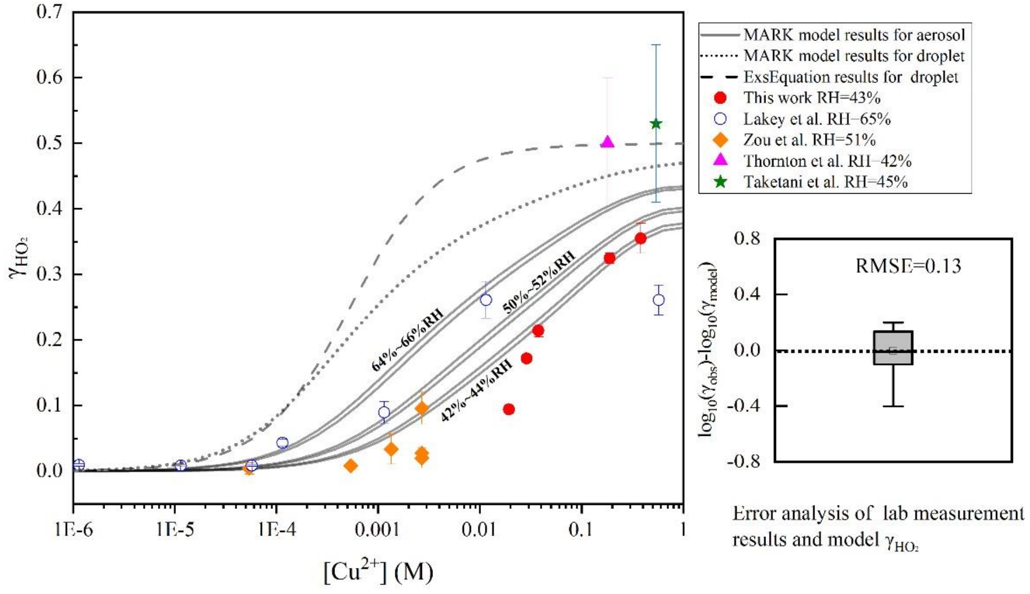

Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red filled circles denote the results at 43% *RH* measured at Leeds included in this paper. Blue hollow circles at 65% *RH* (Lakey et al., 2016c). Yellow filled diamonds denote results at 51% *RH* (Zou et al., 2019), filled purple triangle at 42% *RH* (Thornton and Abbatt, 2005a) and filled green star at 45% *RH* (Taketani et al., 2008). The grey dashed line denotes the results of the existing parameterized equation (named as *CEq.* in this paper) γ_{HO_2} with dilute solution droplets (Thornton et al., 2008; Hanson et al., 1992; Hanson et al., 1994; Jacob, 2000; Kolb et al., 1995), which was confirmed by researches of reactive gas molecular uptake on dilute solution droplets (Hu et al., 1995; Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002). 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%) and the short dotted line represents the result in the MARK model of HO_2 with dilute solution droplets. The root mean square error (RMSE) between the MARK modelled values and the full dataset is 0.13. 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/).

Comment:

1.3 Application of the parameterization (more about the parameterization below): There is a brief discussion of "soluble Cu" in ambient aerosol - but clearly this is the biggest source of uncertainty in using the parameterization. The author's choice of 20% of total Cu being soluble seems rather arbitrary. Really, this issue has been discussed already many years ago - there may well be enough Cu measured in ambient aerosol but whether it is in a soluble form (and also in a "free ion") form remains poorly understood. This uncertainty is compounded by the affect of organic aerosol and its morphology relative to an aqueous phase, the potential for externally mixed aerosol in an urban atmosphere (i.e. the Cu is contained in only a fraction of the total surface area), etc. The authors could show the impact of the various assumptions on the predicted gamma more clearly. Were the Cu measurements size resolved? If so, how does the Cu mass distribution compare to the total aerosol surface area distribution?

Soluble copper concentration is a large source of uncertainty in using the novel parameterization (*NEq.*). There is no measurement of soluble copper concentration in aerosol in the Wangdu campaign. According to the research of Fang et al. (2017), the solubility of Cu across all size ranges of urban aerosol is related to pH. At aerosol pH from 2 to 6, the solubility is about 20%-30%. Based on the previous work mentioned in the MS section 3.4.2, we assume 25% rather than 20% (mentioned as the comments above) of total aerosol metal copper concentration is soluble in the accumulation mode when calculating γ_{HO_2} in Wangdu campaign.

We added the statement in Section 3.5.2 last paragraph in the revised MS: "γ_{HO_2} rather depends on copper concentration so we also evaluate the influence of copper solubility and mixing state of copper in aerosols on the uptake coefficient (details in the SI)."

We test the relation of γ_{HO_2} to copper solubility from 10% to 70% already in the Response to comments at Interactive Discussion. We now added the discussion in the revised SI section 3. We also added the discussion of the mixing state of copper influence on γ_{HO_2} in this part:

"S3 Discussion of the γ_{HO_2} uncertainty when using the *NEq.* in the Wangdu campaign.

S3.2 The uncertainty from the effective copper concentration

We tested the sensitivity of $PM_{2.5}$ 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., 2010a). γ_{HO_2} will increase from 0.065±0.051 at 10% solubility to 0.196±0.142 at 70% solubility for the summary of day and night data based on the Gaussian fitting. The calculation is under the assumption that aerosols are completely *internally mixed*.

The influence of externally mixed aerosol copper on γ_{HO_2} is illustrated below. Since there is no data of copper mixed state in the Wangdu campaign, we assumed a 12 bins distribution of copper concentration to evaluate the influence of Cu mixed state on HO_2 uptake process. The average concentration of Cu is the same as the *internally mixed* one, in which case, 25% copper is soluble in the aerosol particle condensed phase. Cu distributes in the aerosol particles at different concentrations, and the uniformity of the distribution is measured by the Standard Deviation (SD) of its concentration ratio to the averaged Cu concentration. Higher SD means more uneven distribution of Cu in the particles.

This calculation is only valid for particles smaller than 2.5μm (which is the most important size bins for HO_2 uptake), and Cu size distribution in aerosol particles is not considered here. Four modes of external mixtures states were tested as shown in the Table S.6.

Table S.6 Four modes of external mixture state of unbar aerosol copper and corresponding Gaussian fitted γ_{HO_2}.

Gaussian fitted γ_{HO_2}(1σ)	Square Deviation (SD) of the copper distribution
0.110±0.079	0
0.105±0.073	0.35
0.089±0.065	1.18
0.079±0.056	1.71
0.051±0.033	6.24

With the increase of the Square Deviation of copper distribution in aerosol, the uptake coefficient becomes smaller and more centralized. Aerosol particles morphology relative to an aqueous phase will influence the uptake coefficient of HO_2. The uptake process would vary with mixing state and size distribution of the particles, thus the predicted γ_{HO_2} values here may be biased as a result, but represents an average over bulk aerosols. The estimation value of γ_{HO_2} under the assumption that HO_2 reacting with completely *internally mixed* aerosol in the Wangdu campaign is the upper limit value. The uneven distribution of copper in aerosol particles would lead to a further decrease in the HO_2 uptake coefficient. Another source of uncertainty comes from the lack of information about the copper size distribution in Wangdu campaign. This aspect needs further studies.

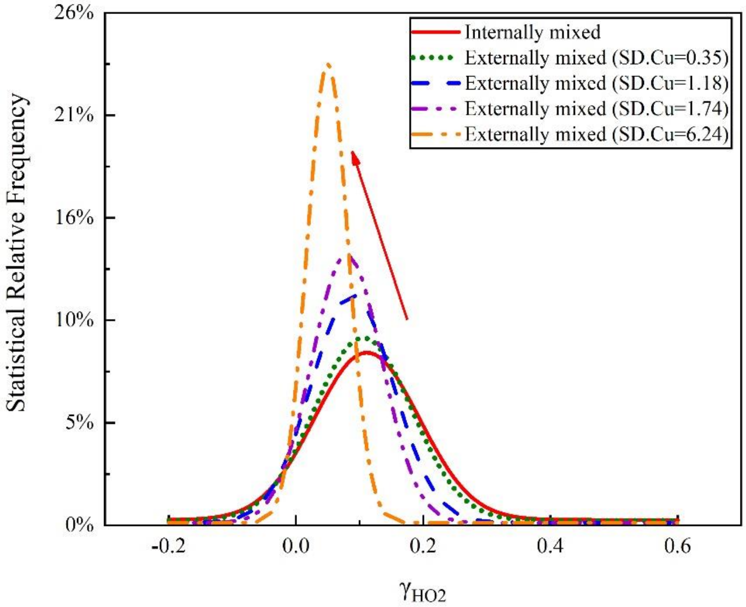

Figure S. 4 The statistical relative frequency distribution of averaged γ_{HO_2} in different modes of copper mix state."

Comment:

What is the organic aerosol mass to inorganic mass ratio? If there was a core-shell morphology and the maximum gamma was similar to the impact of organics on HO2 uptake reported by Lakey et al, what would the current parameterization predict?

We added the following discussion in the revised SI:

"S3 Discussion of the γ_{HO_2} uncertainty when using the *NEq.* in the Wangdu campaign.

S 3.3 The uncertainty from the core-shell morphology of aerosol particles

The presence of organic material would change the value of γ_{HO_2}. We revised the *NEq.* based on the research of Anttila et al. (2006) who treated the organic fraction in the aerosols as a coating, as given below:

$$\gamma_{org\_coat} = \frac{4RTH_{org}D_{org}\varepsilon}{\upsilon_{HO_2}l}$$

$$\frac{1}{\gamma_{HO_2\_corr}} = \frac{1}{\gamma_{HO_2\_in}} + \frac{1}{\gamma_{org\_coat}}$$

Here, the H_{org} is the Henry's law constant of HO_2 for organic coating. D_{org} is the solubility and diffusivity of HO_2 in the organic coating, the value is corrected by Lakey et al. (2016b) using the Stokes–Einstein equation resulting a factor of 1.22 decrease in the diffusion coefficients of HO_2 compared to the diffusion coefficients of H_2O on the sucrose aerosol particles. ε

is the ratio of the radius of the aqueous core (R_c) and the particle (R_d). The particle radius R_d was the measured Count Median Radius of the aerosols [cm]. l is the coating thickness [cm] of the organic matters which is calculated from the volume ratio of the inorganics to total particle volume with the assumption of a hydrophobic organic coating (density, 1.27 g cm^{-3}) on the aqueous inorganic core (with a density of 1.77 g cm^{-3}).

$\gamma_{HO_2\_in}$ and $\gamma_{HO_2\_corr}$ are the uptake coefficients calculated by the *NEq*. and the corrected value under the assumption of organic coating, respectively. We tested the influence of the OM ratios in the range of 20%-70% for HO_2 uptake onto $PM_{2.5}$ due to the lack of direct measurement data in the Wangdu campaign.

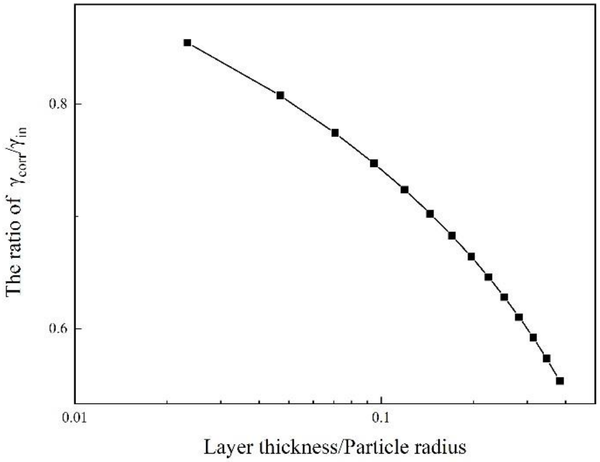

Figure S.5 The ratio of $\gamma_{HO_2\_corr}$ and $\gamma_{HO_2\_in}$ as a function of the relative coating thickness in the Wangdu campaign.

The ratio of $\gamma_{HO_2\_corr}$ and $\gamma_{HO_2\_in}$ decreasing with the ratio of OM denotes the influence of particle core-shell morphology on HO_2 mass transfer process in aqueous organic solvent. Although the diffusion coefficient changes by more than 3 orders (3-7 orders) of magnitude over the investigated range of relative humidity, modeled averaged mean relative difference of HO_2 uptake coefficients change by only 3 times when the l/R_d changes by an order of magnitude. One possible reason for this it is that the uptake coefficient being proportional to the square root of the diffusion coefficient when the uptake is controlled by reaction and diffusion of HO_2 in the bulk (Davidovits et al., 2006; Berkemeier et al., 2013; Lakey et al., 2016a). OM (organic matter) usually accounts for 20–50% mass of $PM_{2.5}$ in Beijing and other urban areas (Wang et al., 2017; Sun et al., 2012). Thus, we proposed a possible range of HO_2 uptake coefficient in the Wangdu campaign as 0.62-0.74 times lower than values without correction for organic matter."

Comment:

Aerosol pH is likely rather uncertain, the authors should discuss a reasonable estimate of uncertainty in the ambient aerosol pH and its size dependence and how this uncertainty would impact the predicted HO2 gamma.

Aerosol pH is an important uncertainty in the implication of the *NEq.*. Aerosol pH size distribution is not measured in the Wangdu campaign; thus we used the estimated $PM_{2.5}$ pH using a thermodynamic equilibrium model as aerosol acidity. ISORROPIA II, was the model used to predict aerosol pH. The averaged aerosol pH is 3.41 ± 0.69 (1σ). The averaged diurnal profiles of aerosol pH are given by Liu et al. (2017). The relative error of measured NH_4^+-Na^+-Cl^+-K^+-HNO_3-NH_3-HCl inputted in the ISORROPIA II model is 10%. The uncertainty caused by aerosol pH is already considered in the estimation of γ_{HO_2} in the revised version. We add the following statements in section 3.5.3 in the revised MS:

"…The aerosol pH is calculated using the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) and the averaged value is 3. 41 ± 0.69 (1σ)."

And in the SI section S3:

"…and aerosol liquid water content (±9.1%). Measured aerosol NH_4^+-Na^+-Cl^+-K^+-HNO_3-NH_3-HCl concentrations cause 10% uncertainty."

Comment:

2) Parameterization development. The discussion of how the parameterization was developed is awkward and could at least use a different organization and in some cases more precise language.

After the last major revision, the manuscript does have local structural confusion and language coherence problems in origin section 3.2. We now rewrite this part and added a new section (section 3.3) to discuss the different applications of the classical equation and the MARK model in the revised MS:

"The classical parameterized equation (*CEq.*) (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.) has been proved to provide good estimation of reactive gas molecular uptake coefficient on dilute solution droplets (Hu et al., 1995; Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002):

$$\frac{1}{\gamma_{HO_2}} = \frac{1}{\alpha_{HO_2}} + \frac{\upsilon_{HO_2}}{4H_{corr}RT\sqrt{D_{aq}k_{TMI}[TMI]}[coth(\frac{R_d}{l_{rd}}-(\frac{l_{rd}}{R_d}))]} \tag{15}$$

$$l_{rd} = \sqrt{\frac{D_{aq}}{k_{TMI}[TMI]}} \tag{16}$$

When the classical parameterized equation (*CEq.*) is applied to the calculate HO_2 uptake coefficient with aerosol, *CEq* has higher deviation of γ_{HO_2} between the measured results compared to the MARK model. All input parameters are the same except that the MARK model involved more liquid phase reactions instead of only considering the second order rate coefficient (k_{TMI}) of HO_2 and O_2^- with transition metal ions as the *CEq.* did. k_{TMI} is the most important parameter in the calculation of uptake coefficient. Based on the research by Bielski in 1985 (Bielski et al., 1985), we used the effective rate constant of HO_{2_total} (=$HO_{2(aq)}$+ $O_2^-{}_{(aq)}$) 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} considering the pH limitation (pH is about 3-5 in ambient aerosol particle condensed phase as discussed 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 (1×10^9 M^{-1} s^{-1}) 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 in the *CEq.* as shown in the dashed line in Figure 2.

IUPAC (Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.) proposed the effective rate coefficient k^1 for the reaction of HO_{2_total} (=$HO_{2(aq)}$+ $O_2^-{}_{(aq)}$) with Cu ions as 5x10^5 M^{-1} s^{-1} to achieve the best fit based on the calculation results from Lakey et al. (2016c). 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 reaction rate of Cu^{2+} with HO_2/O_2^- is 1×10^8 and 8×10^9 M^{-1} s^{-1} in the MARK model. We also test the MARK model with dilute solution droplets as shown in Figure 2 the short-dotted line.

The classical parameterized equation (*CEq.*) is more applicable to calculate uptake coefficient of reactive gas molecular with diluted solution droplets such as cloud or rain droplets. The MARK model uses the same framework with the *CEq.* and considered more parameters influencing uptake process such as the activity coefficients of reactive reagents and the effects of valence states in aerosol particle condensed phase. Considering the small RMSE between the MARK model and the laboratory studies, we proposed a novel parameterized equation (*NEq.*) to better describe the influence of [Cu^{2+}] and *RH* on γ_{HO_2}.

”

The authors should focus on the conditions and parameters which have the biggest effect first. For example, the authors do not mention the rate coefficients used to determine "keff" until the results section! In fact, the entire paragraph on the rate constants needs to be rewritten - I couldn't understand it. The authors open the paragraph saying: "The deviation of $\gamma HO2$ between the MARK model and laboratory studies is smaller than the predicted results from the existing parameterized equation (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.) as shown in Figure 2. " But, it turns out to be closer to the measurements because the authors appear to have chosen a much smaller reaction rate coefficient? Please make that clear - what is the default prediction of the MARK model without any changes to achieve better agreement?? That prediction should be shown on the figure somehow. Then the discussion of what the rate constants are in the literature and what the recommended values are should be discussed clearly - please distinguish HO2(total) from HO2(aq) and O2-(aq). I assume the dissolved forms are treated separately in the model. Basically - it seems the authors are arguing the rate coefficient for various forms of HO2 in a concentrated aqueous solution are different from previous values, and they should present that clearly and why they think those rate constants are actually two orders of magnitude slower and not that the measurements of gamma-HO2 are biased low or low for some other reason (e.g solubility or diffusion limitation, etc). The authors then state at the end: "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 HO2 and the effects of reactions of different valence states of copper ions." This doesn't seem right if you changed the rate constant by two orders of magnitude - I would say that is the main difference between the original parameterization - please demonstrate that the change in this rate constant is not what affects the difference between the MARK and original parameterization (which I assume refers to the dashed line on figure 2).

We change the relative statement in the revised MS to make it clearer that we did not choose a smaller reaction rate coefficient in the MARK model calculations. All the reactions used in the MARK model is presented in the supplementary materials Section 1 Reaction mechanism and reaction rate constants. The reaction rate of Cu^{2+} with HO_2/O_2^- is 1×10^8 M^{-1} s^{-1} and 8×10^9 M^{-1} s^{-1}. All input parameters are the same except that for the MARK model involved more liquid phase reactions instead of only considering the second order rate coefficient (k_{TMI}) for the reaction of HO_2 and O_2^- with transition metal ions as the *CEq.* did. Based on the research of Bielski in 1985 (Bielski et al., 1985), we reduced the input rate constant to 1.5×10^7 M^{-1} s^{-1} rather than the more commonly used value of 1×10^9 M^{-1} s^{-1} (relative discussions are in the MS). This treatment within the calculation can bring predictions more in line with experimental results in the *CEq.*. The *CEq.* can provide good estimation of reactive gas molecular uptake coefficient on dilute solution droplets (Hu et al., 1995; Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002), while may overestimate the uptake coefficients with ambient aerosol (please see the previous response).

Comment:

The authors compare the model predictions of gamma HO2 to the data measured on ammonium sulfate aerosol doped with Cu. What was the assumed pH for the model predictions of the laboratory data? What is the basis of that prediction and could the pH vary between the different laboratory experiments if it wasn't explicitly measured? A flow tube that isn't regularly cleaned could develop and NH3 background which makes the pH possibly higher than estimated for ammonium sulfate in the absence of excess ammonia.

The main components of the aerosols used in the laboratory measurements of γ_{HO_2} shown in Figure 2 are ammonium sulfate with 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°C. In the MARK model, we set aerosol pH as 4.5 when calculating γ_{HO_2}. We also input pH as 4.5 in the *CEq.*. The MARK model and the *CEq.* results have no uncertainty from pH in the calculations. The accurate measurement or calculation of aerosol pH is an important factor in the implication of the novel parameterization (*NEq.*) proposed in this paper as described above.

In the experimental measurements included in this paper a careful procedure for cleaning the aerosol flow tube was used as mentioned above that could also avoid a NH_3 background.

Comment:

The authors discuss that they assumed only HO2 was reacting with Cu in these experiments (at least that is what I discerned - but the language in this section is very unclear as it mentions pH of ambient aerosol being typically 3-6 and so they used the HO2 + Cu rate constant which is two orders of magnitude smaller than O2- + Cu).

The *CEq.* is assuming that only HO_2/O_2^- are reacting with Cu^{2+} ions rather than the MARK model. The MARK model is a box model with lots of other reactions described in detail in the SI Section 1. The MARK model considered other factors such as the activity coefficient and effective Henry's constant. A low reaction rate constant is used in the calculation of the *CEq.* but not in MARK model. Please see response above.

Comment:

The authors mention that the "model selects a mass accommodation coefficient of 0.5" - but this is an input to the model, correct? Is the model prediction iterated for each measurement or how is it that the model selects? The mass accommodation coefficient alone is another source of significant uncertainty - the authors could better illustrate the true uncertainty of the model predictions based on mass accommodation and pH assumptions.

The HO_2 mass accommodation coefficient (α_{HO_2}) is chosen as 0.5 based on the previous work mentioned in Section 2.4. This is an input value to the MARK model as well as in the *CEq.* calculations of γ_{HO_2} with copper-doped ammonium sulfate aerosol. An important reason for choosing 0.5 as the fixed value is that for the copper-doped ammonium sulphate aerosol, when the concentration of copper ion is high enough, the heterogeneous uptake process of HO_2 is mainly limited by mass transfer rate rather than liquid phase chemical reaction rate, which shows the effect of α_{HO_2}. On the other hand, according to the resistance model theory α_{HO_2} does not influence the liquid phase reactants' reaction rates. In the process of optimizing the comprehensive liquid phase reaction rate coefficient k_{eff} the influence of α_{HO_2} on the uptake coefficient can be embodied in the term of $1/\alpha_{HO_2}$, thus there is no correlation between k_{eff} and α_{HO_2}.

The uncertainty of α_{HO_2} mainly manifests in the implication of the *NEq.*. We modified the original text and set three gradients of α_{HO_2} to simulate the uptake coefficient: 0.2, 0.5 and 0.8. We added the following part in the revised SI:

"S3 Discussion of the γ_{HO_2} uncertainty when using the *NEq.* in the Wangdu campaign.

S3.1 The uncertainty from the HO_2 mass accommodation coefficient (α_{HO_2}).

The HO_2 mass accommodation coefficient (α_{HO_2}) is influenced by many factors including the aerosol organic component, particle size distribution, RH and temperature, etc. There is no direct measurement result of α_{HO_2} in the Wangdu campaign or any other field campaign currently due to experimental difficulties. α_{HO_2} is a source of significant uncertainty when using the *NEq.* to estimate γ_{HO_2}. Here we set five gradients of α_{HO_2} to simulate the mean γ_{HO_2} and the results of the fit to a Gaussian function result in γ_{HO_2} median values of 0.088 ± 0.022 (1σ) at α_{HO_2}= 0.2 and 0.125± 0.041 (1σ) at α_{HO_2}= 0.8.

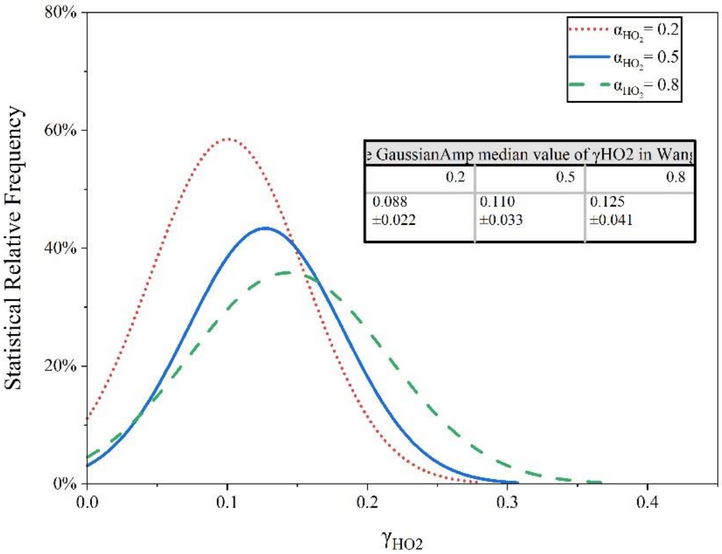

Figure S.3 Gaussian fitting results of γ_{HO_2} under different α_{HO_2} in the Wangdu campaign, estimated by the *NEq.*."

Comment:

3) Presentation - as noted in the above comments, more clarity is needed in what assumptions are made, under what conditions, and what the impact of those assumptions is on the main conclusions.

I find little need to show the distribution of gamma values for day and night - the two distributions look essentially the same. The only different is that HO2 reactive uptake becomes a larger fraction of the total HOx loss (because RO2 + NO goes towards zero). This seems a minor distinction to make given the bigger uncertainties in the applicaiton of the parameterization as discussed above that would be better to communicate to the broader community that might want to employ the parameterization.

We deleted the panel (a) and (b) in Figure 4 now and give the Gaussian fitted value of HO_2 uptake coefficient for the summary of day and night data.

A new section “3.5.4 Discussion of uncertainties of γ_{HO_2} estimated at Wangdu field campaign” in the revised MS has been included that discussed the uncertainties of the *NEq.* proposed by this paper.

The value estimated by the *NEq.* represents the upper limitation of γ_{HO_2} in the Wangdu field campaign considering the large uncertainties mainly from the aerosol properties. More work needs to be done to evaluate the true value of γ_{HO_2}. The *NEq.* proposed by 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.

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Influence of aerosol copper on HO_2 uptake: A novel parameterized equation

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Abstract. ~~The heterogeneous~~Heterogeneous uptake of ~~hydroxyl peroxy~~hydroperoxyl radicals (HO_2) ~~on aerosol~~onto aerosols has been proposed to be a significant sink of HOx~~, thus could influence~~ ~~and~~ hence ~~it affects~~impacting the atmospheric oxidation capacity. Accurate calculation of the HO_2 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 changes in aerosol properties, especially ~~those of~~ aerosol soluble copper (Cu) concentration and aerosol liquid water content (ALWC). In this study~~,~~ we ~~develop~~present a state-of-the-art model called MARK to simulate both gas and aerosol phase chemistry~~. A novel parameterized equation~~ for the uptake of HO_2 ~~considering change in RH and aerosol~~onto Cu~~ is~~ -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 ~~toward all available lab experiments.~~ using previously published laboratory and new laboratory data included in this work. This new parametrization would be applicable to wet aerosols and it would complement current IUPAC recommendation for cloud droplets. The new parameterization is as follows:

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

~~According to the new equation, highly variable HO_2 uptake coefficients (median value~0.1) were diagnosed for North China Plain and the impact of HO_2 uptake on the ROx budget is assessed.~~

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

All parameters used in the paper are summarized in Table A1. ~~].],.PM~~~~RH~~~~relative humidity (0-1)mass concentration of particles [μg m^{-3}].,.The H_{org} is the Henry's law constant of HO_2 for organic coating,. D_{org} is the solubility and diffusivity of HO_2 in the organic coatingε is the ratio of the radius of the aqueous core (R_c) and the particle (R_d). l is the coating thickness [cm] of~~

~~the organic matters which is calculated from the volume ratio of the inorganics to total particle volume with the assumption of a hydrophobic organic coating (density, 1.27 g cm^{-3}) on the aqueous inorganic core (with a density of 1.77 g cm^{-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.~~Using this new equation, field data from Wangdu campaign were used to evaluate the impact of the HO$_2$ uptake onto aerosols on the ROx (=OH + HO$_2$+RO$_2$) budget. Highly variable values for HO$_2$ uptake were obtained for North China Plain (median value <0.1).

1 Introduction

The atmospheric clean~~s~~ing 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)~~ (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)~~ (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 spans several orders of magnitude, ranging from <0.002 for dry aerosols (Cooper and Abbatt, 1996; Taketani et al., 2008; George et al., 2013) to 0.2 for ~~neutralized~~liquid deliquesced aerosols(Thornton and Abbatt, 2005b)~~.~~. Much higher values of γ_{HO_2} have been measured and calculated for Cu-doped aerosols (Mozurkewich et al., 1987; Taketani et al., 2008; Thornton et al., 2008; Cooper and Abbatt, 1996; Lakey et al., 2016c; 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 HO_2 uptake on ~~worrisome and~~ pressing atmospheric issues such as ozone formation.

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

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~~laboratory experiments. The reaction mechanism and reaction rate constants are summarized in Table S.1 – S.4 in the Supplementary Information (SI). The MARK model is currently capable of simulating inorganic deliquescent aerosol at ambient pressure and temperature. The model directly calculates the ~~net~~quasi-first order gas phase uptake loss rate, ~~k_{het},~~ k_{het} (s^{-1}), in Eq. (1). In this model, aerosol liquid water content (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).

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

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

~~where r_p is the aerosol particle radius[cm], $\bar{v}$ is the mean molecular speed of HO_2 [$cm^{-}s^{-1}$]. and D_g is the gas phase diffusion coefficient [cm^2s^{-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^{ee} 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).~~ The units of aqueous reagents are converted to [molecule cm^{-3}] in the model by k_{mt}. ~~An approach to~~To combine both gas phase molecular diffusion and liquid phase interface mass transport processes the approach adopted is using ~~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~~is given by equation (3):

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

~~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 $k_{mt\_X} \times ALWC$ (where *X* is the reactant molecule). Moreover, the conversion rate of aqueous phase reactants to gas phase can be calculated as $\frac{k_{mt\_X}}{H^{cc} \times RT}$. 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 >1μm), k_{mt} is mainly determined by gas phase diffusion of HO_2. For smaller particles (radius <1μm) k_{mt} is mainly determined by the accommodation ~~coefficient~~ process~~(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. Consequently, ~~in which~~ an effective Henry's law constant H^{cc} should be applied in the model calculation, that takes into account ~~considering~~ the effects of solution pH and ~~the small gas phase molecule (such as HO_2, OH, O_2 ect.)~~ "*salting out*" effect in the small gas phase molecule (such as HO_2, OH, O_2 ect.) due to the existence 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).

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 HO2[mol cm − 3 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 ~~equilibrium constant for HO_2 in the gas phase. Activity coefficient A for HO_2~~pH and ~~other neutral small molecule can be expressed as(Ross and Noone, 1991):~~ the "*salting out*" effect. In the MARK model, these two corrections are incorporated as H^{cc} ~~H^{cc}~~:

$$H^{cc} = H_0 \times \cancel{\left(1+\frac{k_{eq}}{[H+]}\right)} \left(1+\frac{K_{eq}}{[H+]}\right) \times A_{HO_2} \cancel{(3} = 9.5 \times 10^{-6}\, exp\left(\frac{5910}{T}\right) \times \left(1+\frac{K_{eq}}{[H^+]}\right) \times A_{HO_2}$$ (4)

The activity coefficient *A* for HO_2 and other neutral small molecules such as H_2O_2 and O_2 can be expressed as (Ross and Noone, 1991):

$$AA_{\cancel{HO_2}} = 10^{-0.1\times I}$$ (~~4~~5)

~~In MARK model, the effective Henry's constants of main gas phase reactant are corrected based on above equations.~~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^{2+} concentration.

2.2.2 Aerosol ~~bulk~~particle condensed phase 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~~ since 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~~, consequently the activity coefficient ~~to modify the ion concentration. Therefore, 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~~ Based on Ross and Noone (Ross and Noone, 1991), for an ion (x_i) of charge z_i (i=x,y,z…), the activity coefficient (φ_x) is

$$\cancel{log \varphi x = -z_x^2}\, log\, \varphi_x = -z_x^2 D - \sum_y \varepsilon(x,y,I) m_y$$ (~~5~~6)

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

$$D = \frac{0.5109\sqrt{I}}{1+1.5\sqrt{I}}$$ (~~6~~7)

~~Where m_y is the molality of an ion [mol L^{-1}],~~ *I* is the i~~r~~onic strength of a solution [~~mol L^{-1}~~M], which can be calculated as following equation:

$$I = \frac{1}{2} \cdot \sum m_i \cdot z_i^2 \tag{~~7~~8}$$

~~$\varepsilon(x,y,I)$ 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 $\log(A_\pm)$ (Clegg et al., 1998) of the single electrolyte ($\log(A_\pm)$) at the same I where~~ $\varepsilon(x,y,I)$ 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, $\varepsilon(x,y,I)$ is set to zero. For ions of unequal charge, $\varepsilon(x,y,I)$ may be calculated from the logarithm solution mean activity coefficient $log(A_\pm)$ (Clegg et al., 1998) of the single electrolyte at the same *I* according equation (9):

$$\varepsilon(x,y,I) = \cancel{\frac{(\log(A_\pm)+z_x z_y D)(z_x+z_y)^2}{4I}}\,\frac{(log(A_\pm)+z_x z_y D)(z_x+z_y)^2}{4I} \tag{~~8~~9}$$

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

$$[x_i]_{equ} = [x_i] \times \cancel{\varphi x(9} \ \varphi_x \qquad (10)$$

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~~-~~:

$$[Cu^{2+}]_{equ} = [Cu^{2+}] \times \cancel{\varphi_{Cu^{2+}}}\ \varphi_{Cu^{2+}} \tag{11}$$

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

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

Gas phase HO$_2$ molecules dissolve in the ~~bulk~~particle condensed phase and diffuse from the surface of a particle toward the center ~~coupled~~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. $[HO_{2(\mathrm{r})}]$ is HO$_2$ concentration at the surface~~.~~ of particles. The ratio of these two concentrations can be calculated as~~(Schwartz and Meyer, 1986)~~ (Schwartz, 1986; Schwartz, 1984):

$$\cancel{\frac{[\overline{HO_2}]}{[HO_{2(\mathrm{r})}]}}\,\frac{[\overline{HO_2}]}{[HO_{2(r)}]} = 3 \times \left(\frac{coth(q)}{q} - \frac{1}{q^2}\right) \tag{~~10~~12}$$

where q is given by equation (13):

$$q = \cancel{r_p} R_d \times \left(\frac{k_{eff}}{D_{aq}}\right)^{0.5} \qquad (1~~1~~3)$$

~~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}~~].~~], k_{eff} is the comprehensive liquid phase 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~~1μm), the ratio ~~is approximately equal~~ $\frac{[\overline{HO_2}]}{[HO_{2(r)}]}$ is close to 1~~ (higher~~. At a diameter of 1μm, 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~~ at 200nm diameter particle based on the calculation) .~~. 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 ~~bulk~~condensed phase average HO_2 concentration.

2.3 Laboratory results for the HO_2 accommodation coefficient

The accommodation coefficient of HO_2 used in the model was determined for copper-doped inorganic aerosol ~~in~~particles using values taken from various previous ~~lab~~laboratory 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 cataly~~s~~t~~i~~is~~s~~c effect of Cu^{2+} on aqueous HO_2/~~-~~O_2^- (Table 1). In this situation, the aqueous reactions are fast enough ~~that~~for the uptake process ~~is~~be 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 radicals. 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 ~~α~~α_{HO_2} as 0.5. We also tested the influence of the accommodation coefficient on calculated HO_2 uptake coefficient in a field campaign, details please see the Supplementary Information.

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

Aerosol type	RH/%	Estimation of [Cu] in aerosol (mol L-1)	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, 2005a)
$(NH_4)_2SO_4$	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., 2016c)
$(NH_4)_2SO_4$	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)

ation of [Cu] in osol (mol L^{-1})	
059−0.067*	0.4
0.5	0.5
0.16	0
0.5−0.7*	0
0.57	0.2
0.0027	0.09
0.38	0.35
~0.5	0.6
f KCl solution	0.5
03−0.0063*	0.

~~Aerosol type~~	~~*RH*/%~~	~~Estimation of [Cu] in aerosol/M~~	~~*α*~~	~~Ref.~~
~~NH$_4$HSO$_4$~~	~~75%~~	~~0.0059~0.067~~	~~0.40±0.21~~	~~Mozurkewich et al.(Mozurkewich et al., 1987)~~
~~(NH$_4$)$_2$SO$_4$~~	~~45%~~	~~0.38~~	~~0.53±0.12~~	~~Taketani et al.(Taketani et al., 2008)~~
~~(NH$_4$)$_2$SO$_4$~~	~~42%~~	~~0.16~~	~~0.5±0.1~~	~~Thornton and Abbatt~~(Thornton and Abbatt, 2005b; Thornton and Abbatt, 2005a)
~~(NH$_4$)$_2$SO$_4$~~	~~55%~~	~~0.34~~	~~0.5±0.3~~	~~Moon~~(Moon et al., 2018a; George et al., 2013)
~~(NH$_4$)$_2$SO$_4$~~	~~53~65%~~	~~0.5~0.7~~	~~0.4±0.2~~	~~George et al.~~(Lakey et al., 2016c)
~~NaCl~~	~~53%~~	~~~0.5~~	~~0.65±0.17~~	~~Taketani et al.(Taketani et al., 2008)~~
~~KCl~~	~~75%~~	~~5% of KCl solution~~	~~0.55±0.19~~	~~Taketani et al.(Taketani et al., 2009)~~
~~LiNO$_3$~~	~~75%~~	~~0.03~0.063~~	~~0.94±0.5~~	~~Mozurkewich et al.(Mozurkewich et al., 1987)~~

*Cu concentration is in molality (M).

2.4 ~~Reaction mechanism~~The experimental setup and ~~reaction rate~~ methodology of the latest results of γ_{HO_2}~~γ_{HO_2}~~

In this study, we also~~o~~ conclude the latest results which measured at Leeds. The experimental setup and methodology used to make the new measurements of $\gamma(HO_2)$ reported here have been described in detail elsewhere (Moon et al., 2018b; Lakey et al., 2016c; George et al., 2013) and so only brief details are given here. In summary, the experiments were performed by moving an HO_2 injector backwards and forwards along the concentric axis of a laminar aerosol flow tube hence changing the contact time between HO_2 and the aerosols. Measurements of $[HO_2]$ were performed using laser induced fluorescence (LIF) spectroscopy at low-pressure (the fluorescence assay by gas expansion (FAGE) technique (Heard and Pilling, 2003)) and the total aerosol surface area was determined with a Size Mobility Particle Sizer (SMPS) at the end of the flow tube. Aerosols were formed using a constant output atomiser (TSI, 3076) and the aerosol concentration and hence surface area could be varied, being controlled using a high efficiency particulate air (HEPA) filter in a bypass arrangement. Atomiser solutions were prepared by dissolving 0.01 moles of ammonium sulphate (AS) (Fisher scientific, >99%) with varying amounts of copper (II) sulphate (Fisher scientific, >98%) in 500 mL of Milli-Q water. The data were analysed as described in George et al 2013. The pseudo first-order loss rate coefficient (k') was obtained from the gradient of a plot of ln(HO_2 signal) against the interaction time between HO_2 and the aerosol before sampling by the FAGE detector. The uptake coefficient ($\gamma(HO_2)$) was obtained from the linear least-squares gradient of the plot of k' against the surface area concentration of aerosols in the flow tube. The error given on all measurements of $\gamma(HO_2)$ represents 2σ of the uncertainty of the fitted gradient. A correction to k' was applied to taking into account non-plug flow conditions in the flow tube using the Brown method.

~~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.~~

~~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~~	~~$Cu^{2+} + HO_{2(aq)} \longrightarrow Cu^{+} + H^{+} + O_{2(aq)}$~~	~~$1\times10^{8*}$~~	
~~R9~~	~~$Cu^{2+} + O_2^- \longrightarrow Cu^{+} + O_{2(aq)}$~~	~~$8\times10^{9*}$~~	
~~R10~~	~~$O_2^- + O_{3(aq)} \longrightarrow O_{2(aq)} + O_3^-$~~	~~$1.5\times10^{9*}$~~	~~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}~~	

~~*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~~	~~$H_2O_{(aq)} \leftrightarrow H^+ + OH^-$~~	~~1.8×10^{-16}~~	

~~E2~~	~~$HO_{2(aq)} \leftrightarrow H^+ + O_2^-$~~	~~1.6×10^{-5}~~	
~~E3~~	~~$Cu^{2+} + OH_{(aq)} \leftrightarrow CuOH^{2+}$~~	~~1.17×10^{4}~~	
~~E4~~	~~$HO_{3(aq)} \leftrightarrow H^+ + O_3^-$~~	~~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).~~

~~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} ALWC~~
~~T2~~	~~$OH \longrightarrow OH_{(aq)}$~~	~~k_{mtOH} ALWC~~
~~T3~~	~~$O_3 \longrightarrow O_{3(aq)}$~~	~~k_{mtO3} ALWC~~
~~T4~~	~~$O_2 \longrightarrow O_{2(aq)}$~~	~~k_{mtO2} ALWC~~
~~T5~~	~~$H_2O_2 \longrightarrow H_2O_{2(aq)}$~~	~~k_{mtH2O2} 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}]~~	~~-△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~~

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

3 Results and Discussion

3.1 Parameter sensitivity analysis of the MARK model

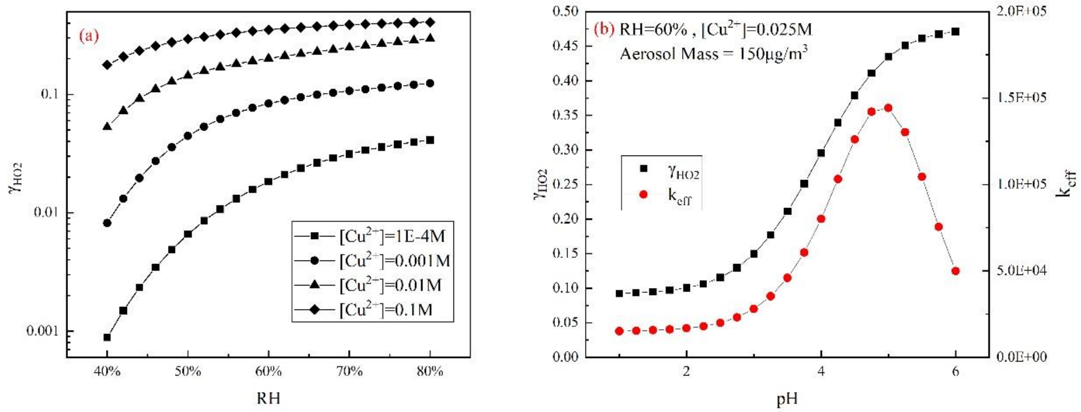
Hygroscopic inorganic ~~particle is~~ particles are one of the most important components of $PM_{2.5}$ in ~~the~~ ambient air. The annual average contribution of inorganic aerosol to $PM_{2.5}$ is between 25% and 48% ~~(Tao et al., 2017)~~across China (Tao et al., 2017), especially NH_4^+, SO_4^{2-}, 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 ~~andin order to~~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., 2016c; 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 actualwithin 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 reactions of HO_2 are ~~is~~ simulated by the MARK model, and good correlation between simulation results and experimental results are obtained especially considering the influence of both [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.~~

Figure 1 shows the influences of both factors,– ~~:~~RH and condensed phase pH together with ~~including~~ Cu^{+2} ~~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$_2$O$_2$.



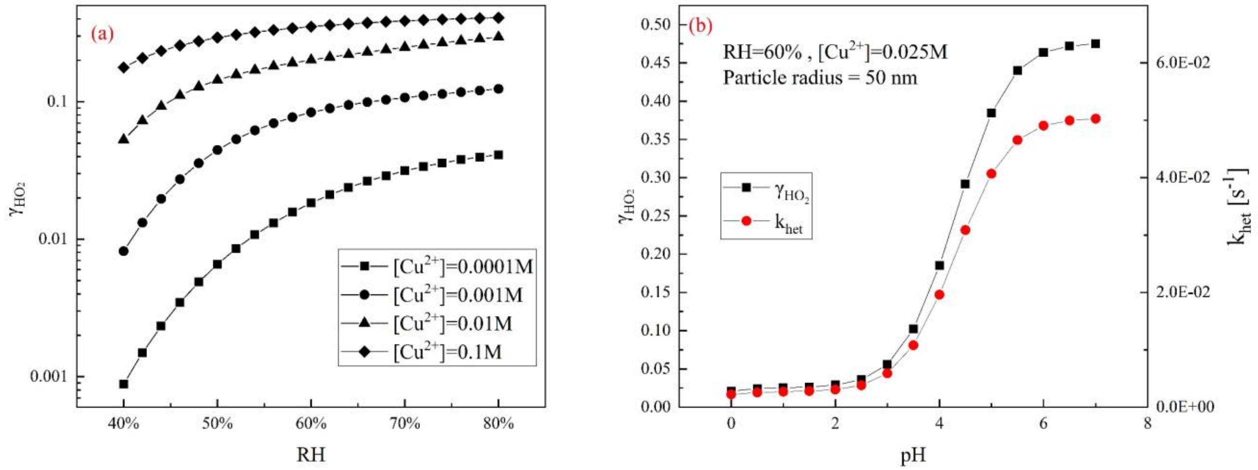


Figure 1: ~~Parameter analysis~~Influence of various parameters upon γ_{HO_2} predicted by the ~~Mark~~MARK model. (a) γ_{HO_2} increases with the *RH* at different [Cu^{2+}]; (b)~~γ_{HO_2} in~~ γ_{HO_2} denoted by black ~~square dotted~~squares and black line ~~increases~~and k_{het} in red circles and red line increase with aerosol ~~bulk~~particle condensed phase pH~~ and k_{eff} in red circular dotted line has a peak value at about pH=5 then declines quickly~~.

γ_{HO_2} ~~has an S~~presents a sigmoid-shaped growth with aerosol ~~bulk~~particle condensed 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.~~ In the model, it is found that as the pH ris~~ing~~es, 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~~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 ~~indicatingmay~~ mainly because of the ~~significance of this field of study~~change of HO_2 solubility.

3.2 Model V~~er~~al~~i~~fi~~c~~dation

~~In the existing γ_{HO_2} parameterized equation~~Although the MARK model simulation results in this paper are not obtained by adjusting parameters to fit the experimental data points, the MARK model fitted well with these results under different ambient RH and Cu^{2+} concentrations.

At present, there are experimental measurements of γ_{HO_2} at different RH (Thornton et al., 2008; Taketani et al., 2008, 2009; Taketani and Kanaya, 2010; Taketani et al., 2012; Matthews et al., 2014; Thornton and Abbatt, 2005a)~~, the quasi-first-order reaction rate K^I equals to $K^H \times [Cu]$, where K^H 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^H 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}.~~

but there is no an experimental systematic study of this dependence where only RH is changed and not other parameters. Many researches proposed that γ_{HO_2} is higher ~~with~~ for aqueous inorganic aerosol than for dry inorganic aerosol. Although the previous experiments did not directly measure the dependence of RH, the change of the uptake coefficient met the simulation trend ~~of our simulation~~ (see Figure 2). For hygroscopic inorganic aerosols, RH significantly affects the aerosol liquid water content, changing its ionic strength, aqueous reagent activity coefficients, and the solubility of the gas phase reactant such as OH, HO_2 and H_2O_2.

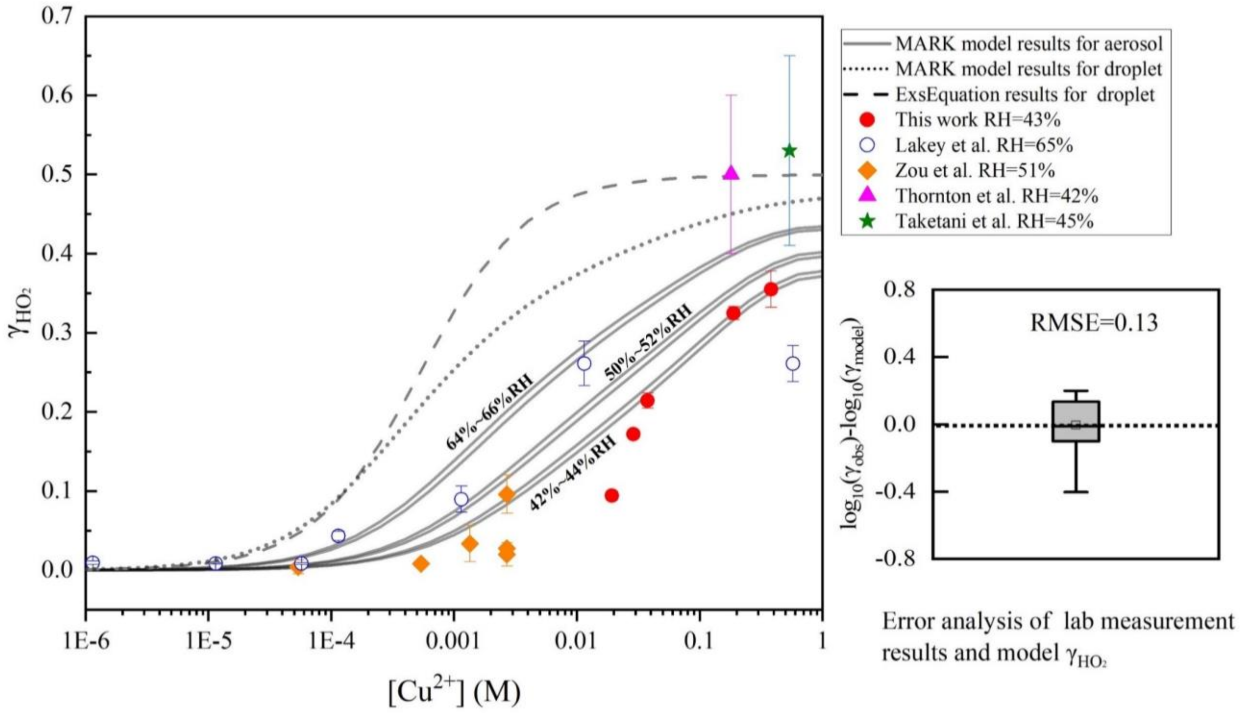
Aerosol condensed phase copper ion concentration is another important factor of HO_2 uptake by adjusting the aqueous reaction rates between HO_2/O_2^- and Cu. As shown in Fig. 2. when the condensed phase copper ion concentration is less than $1\text{-}2\times10^{-4}$ M, the heterogeneous uptake of HO_2 is not significant. This threshold is consistent with the results of ~~previos~~previous researches (Mozurkewich et al., 1987; Lakey et al., 2016c). The tshreshold is also consist in different heterogeneous media of aerosol and droplets. As the copper concentration increases, γ_{HO_2} rapidly rises to the limit of the accommodation coefficient determined by the HO_2 solubility.

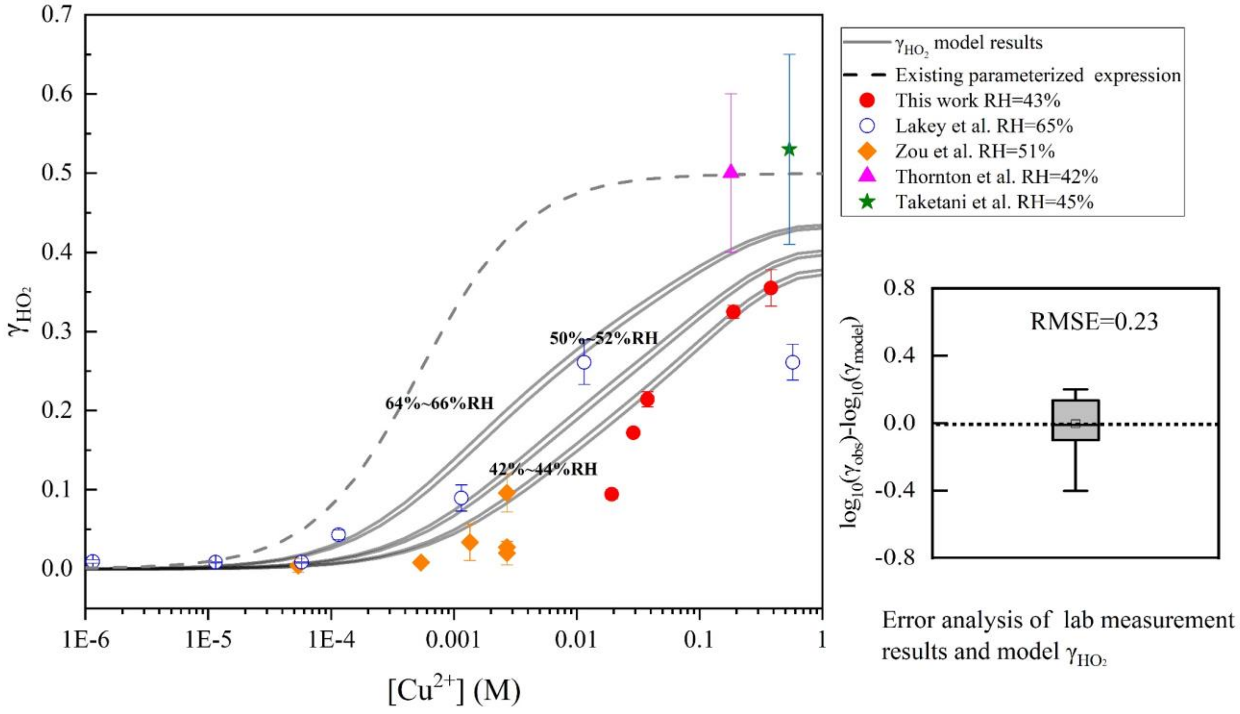
What is more, laboratory measurement uncertainties will directly influence the evaluation of the deviation between the modelled HO_2 uptake coefficient and the measured results because all the parameters inputted in the MARK model are in reference to the measurement conditions. However, it is difficult to calculate~~d~~ the detailed uncertainties from all factors that influence γ_{HO_2} because of the nonlinear reaction system. Uncertainties of the experimental conditions such as RH and particle diameters are combined into the reported values of γ_{HO_2}. Taking all these into account, we calculated an averaged uncertainty for the experimental values of γ_{HO_2} in different ranges of Cu ions concentration. Laboratory measurement uncertainty has the largest value of 35.1% in the range of 1×10^{-4} to 0.01 M soluble copper concentration, 14.9% below 1×10^{-4} M and 9.3% higher than 0.01 M.

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). In this paper, the relative error of each measured data point is considered to calculate the weighted average in RMSE:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}\left(\left(\log_{10}^{u_{i_{measured}}} - \log_{10}^{u_{i_{model}}}\right)^2 (\omega_i)^2\right)}{\sum_{i=1}^{n}(\omega_i)^2 \cdot n}} \qquad (14)$$

$u_{i_{model}}$ is the MARK model result at each Cu^{2+} concentration and *RH*, $u_{i_{measured}}$ is the central value of each measurement result and ω_i is its corresponding relative error.


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
γ_{HO_2}
1E-6
1E-5
1E-4
0.001
0.01
0.1
1
[Cu^{2+}] (M)
64%~66%RH
50%~52%RH
42%~44%RH
MARK model results for aerosol
MARK model results for droplet
ExsEquation results for droplet
This work RH=43%
Lakey et al. RH=65%
Zou et al. RH=51%
Thornton et al. RH=42%
Taketani et al. RH=45%
0.8
0.4
0.0
-0.4
-0.8
$\log_{10}(\gamma_{obs})-\log_{10}(\gamma_{model})$
RMSE=0.13
Error analysis of lab measurement results and model γ_{HO_2}


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
γ_{HO_2}
1E-6
1E-5
1E-4
0.001
0.01
0.1
1
[Cu^{2+}] (M)
64%~66%RH
50%~52%RH
42%~44%RH
γ_{HO_2} model results
Existing parameterized expression
This work RH=43%
Lakey et al. RH=65%
Zou et al. RH=51%
Thornton et al. RH=42%
Taketani et al. RH=45%
0.8
0.4
0.0
-0.4
-0.8
$\log_{10}(\gamma_{obs})-\log_{10}(\gamma_{model})$
RMSE=0.23
Error analysis of lab measurement results and model γ_{HO_2}

~~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., 2018a)). 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, 2005b)~~)~~ ~~and star at 45% RH (research by Taketani et al., 2008(Taketani et al., 2008)). 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., 2018a) and Zou et al., 2019(Zou et al., 2019) is 0.16 indicating a small deviation in MARK model calculations.~~

Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red filled circles denote the results at 43% *RH* measured at Leeds included in this paper. Blue hollow circles at 65% *RH* (Lakey et al., 2016c). Yellow filled diamonds denote results at 51% *RH* (Zou et al., 2019), filled purple triangle at 42% *RH* (Thornton and Abbatt, 2005a) and filled green star at 45% *RH* (Taketani et al., 2008). The grey dashed line denotes the results of the classical parameterized equation ~~existing parameterized equation~~ (named as *CEq.*~~ExsEquation~~ in this paper) γ_{HO_2} with dilute solution droplets (Thornton et al., 2008; Hanson et al., 1992; Hanson et al., 1994; Jacob, 2000; Kolb et al., 1995), which was confirmed by researches of reactive gas molecular uptake on dilute solution droplets(Hu et al., 1995; Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002). 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%) and the short dotted line represents the result in the MARK model of HO_2 with dilute solution droplets. The root mean square error (RMSE) between the MARK modelled values and the full dataset is 0.13. 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/).

3.3 Comparison of the classical ~~parametetized~~parameterized equation and the MARK model

The classical parameterized equation (*CEq.*) ~~As shown in Fig. 2. when the aerosol copper is less than 1~2×10^4M, the heterogeneous uptake of HO_2 is not significant.~~ ~~As the copper concentration increases, γ_{HO_2} rapidly rises to the limits of accommodation and HO_2 solubility. Many research studies have proposed that ambient RH affects γ_{HO_2}~~ (Thornton and Abbatt, 2005b; Thornton et al., 2008; Taketani et al., 2008, 2009; Taketani and Kanaya, 2010; Taketani et al., 2012; Matthews et al., 2014)~~. 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.~~

~~In this study, we used MARK model to simulate the observed γ_{HO_2} from all the available lab studies, which were conducted with different ambient RH and Cu^{2+} concentrations~~(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_2} from both the MARK model and lab studies are much smaller than the predicted results from the existing parameterized equations for [Cu^{2+}] (smaller than 0.1 mol L^{-1}). Therefore, a novel parameterized equation is required to better describe the influence of [Cu^{2+}] on γ_{HO_2}.~~

~~3.3~~ has been proved to provide good estimation of reactive gas molecular uptake coefficient on dilute solution droplets (Hu et al., 1995; Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002):

$$\frac{1}{\gamma_{HO_2}} = \frac{1}{\alpha_{HO_2}} + \frac{\upsilon_{HO_2}}{4H_{corr}RT\sqrt{D_{aq}k_{TMI}[TMI]}[coth(\frac{R_d}{l_{rd}}-(\frac{l_{rd}}{R_d}))]} \qquad (15)$$

$$l_{rd} = \sqrt{\frac{D_{aq}}{k_{TMI}[TMI]}} \qquad (16)$$

When the classical parameterized equation (*CEq.*) is applied to the calculate HO_2 uptake coefficient with aerosol, *CEq* has higher deviation of γ_{HO_2} between the measured results compared to the MARK model. All input parameters are the same except that the MARK model involved more liquid phase reactions instead of only considering the second order rate coefficient (k_{TMI}) of HO_2 and O_2^- with transition metal ions as the *CEq.* did. k_{TMI} is the most important parameter in the calculation of uptake coefficient. Based on the research by Bielski in 1985 (Bielski et al., 1985), we used the effective rate constant of $HO_{2\ total}$ (=$HO_{2(aq)}$+ $O_2^-{}_{(aq)}$) 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} considering the pH limitation (pH is about 3-5 in ambient aerosol particle condensed phase as ~~dicussed~~discussed 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 (1×10^9 M^{-1} s^{-1}) 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 in the *CEq.* as shown in the dashed line in Figure 2.

IUPAC (Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.) proposed the effective rate coefficient k^1 for the reaction of $HO_{2\ total}$ (=$HO_{2(aq)}$+ $O_2^-{}_{(aq)}$) with Cu ions as 5x10^5 M^{-1} s^{-1} to achieve the best fit based on the calculation results from Lakey et al. (2016c). This assumption is not in accordance with the aqueous reaction rate coefficient from other databases mentioned ~~below, and~~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 reaction rate of Cu^{2+} with HO_2/O_2^- is 1×10^8 and 8×10^9 M^{-1} s^{-1} in the MARK model. We also test the MARK model with dilute solution droplets as shown in Figure 2 the ~~short dotted~~short-dotted line.

The classical parameterized equation (*CEq.*) is more applicable to calculate uptake coefficient of reactive gas molecular with diluted solution droplets such as cloud or rain droplets. The MARK model uses the same framework with the *CEq.* and considered more parameters influencing uptake process such as the activity coefficients of reactive reagents and the effects of valence states in aerosol particle condensed phase. Considering the small RMSE between the MARK model and the laboratory studies, we proposed a novel parameterized equation (*NEq.*) to better describe the influence of $[Cu^{2+}]$ and *RH* on γ_{HO_2}.

3.~~3~~ 4 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 Freiberg, 1981; Schwartz, 1987):

$$HO_{2(g)} \rightleftharpoons HO_{2(r)} \rightleftharpoons HO_{2(a)} \xrightarrow{k_{eff}} Products \qquad (\cancel{12}174)$$

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^{+}] 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~~$_{\cancel{2}}$~~]~~$[HO_{2(r)}]$ 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~~discussed 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 (*NEq.*) 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.~~:

$$\frac{1}{\gamma} = \frac{1}{\alpha_{HO_2}} + \frac{3\times\upsilon_{HO_2}}{4\times R_d\times H_{corr}\times RTk_{eff}} \qquad (18\cancel{5})$$

$$k_{eff} = f(\mathrm{ALWC},\mathrm{PM}) \times [Cu^{2+}]_{equ} \qquad (19\cancel{6})$$

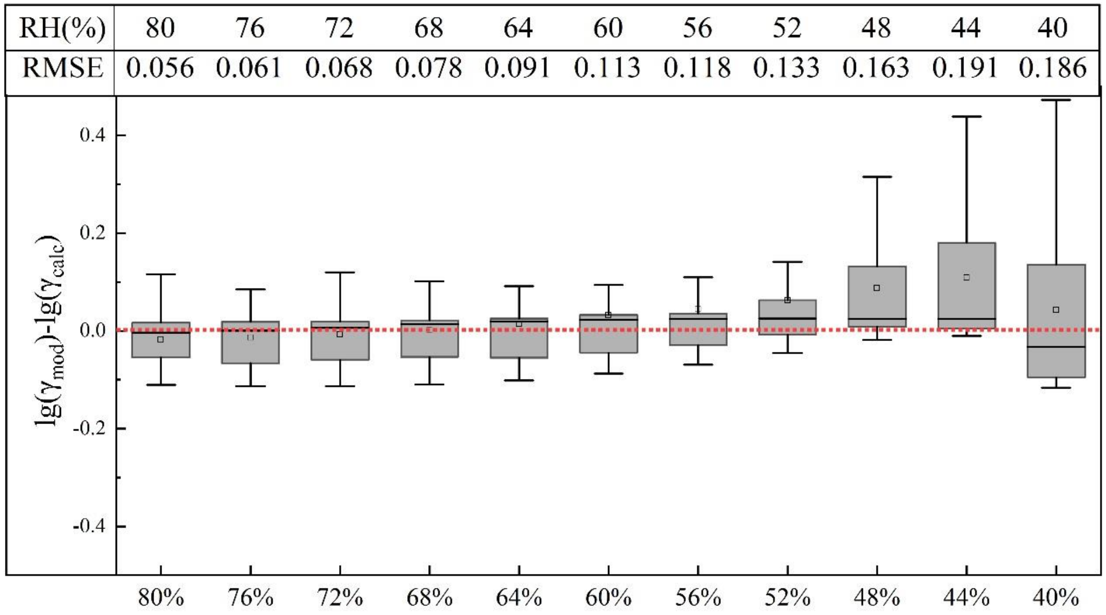
$$f(\mathrm{ALWC},PM) = 10^6 \times (5.87 + 3.2 \times ln\left(\frac{\mathrm{ALWC}}{[\mathrm{PM}]} + 0.067\right)) \times [\mathrm{PM}]^{-0.2} \qquad (20\cancel{17})$$

$$[Cu^{2+}]_{equ} = [Cu^{2+}]^{\varphi} = [Cu^{2+}]^{0.65} \qquad (21\cancel{18})$$

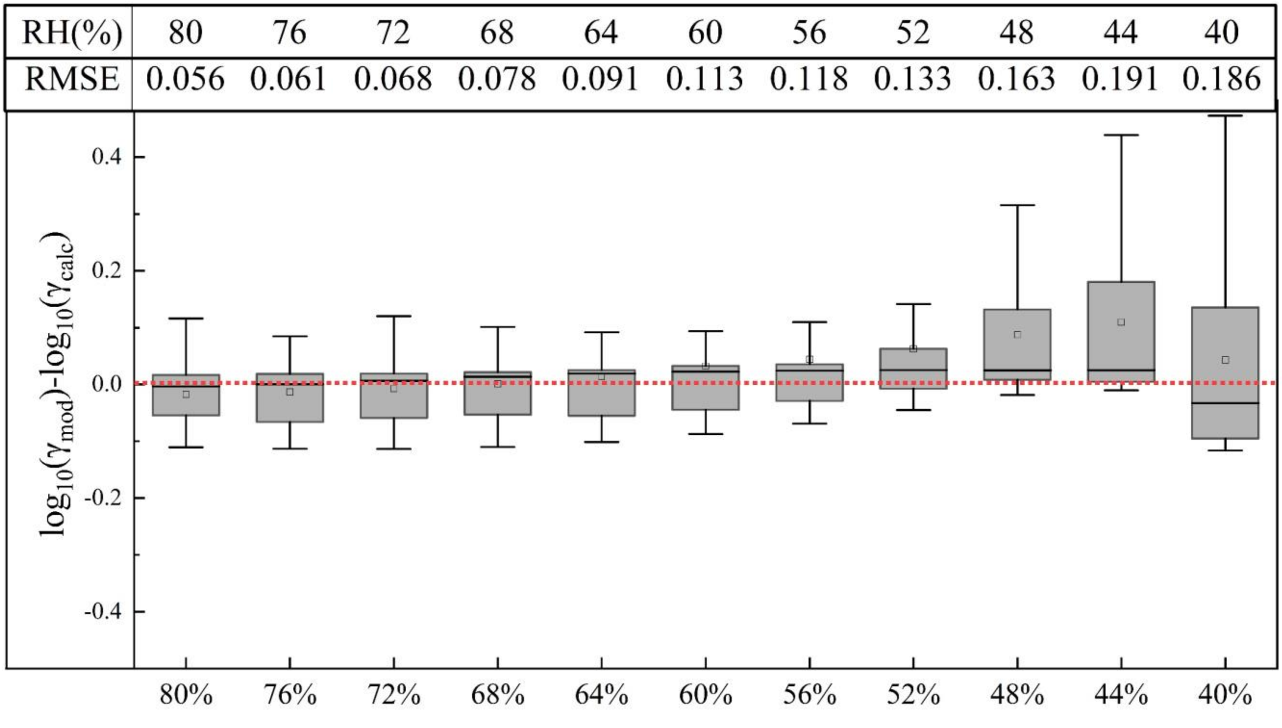
From Eq. (18~~5~~), it can be deduced that γ_{HO_2} can be calculated by optimizing k_{eff} under different ambient environmental conditions from the MARK model results. The MIPFIT model(Markwardt, 2009; Lewis et al., 2009) (Markwardt, 2009; Lewis et al., 2009) in the IDL software program is used to 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_2} 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~~19~~6~~). 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. $f(\mathrm{ALWC}, [\mathrm{PM}])$ has a negative exponential relationship to [PM], and has a positive linear relationship to *RH*. $[Cu^{2+}]_{equ} = [Cu^{2+}]^{\varphi} = [Cu^{2+}]^{0.65}$ ~~(17)~~

We further calculated the RMSE of the modeled data and *NEq.*(Eq.15) ~~parameterized equation (185)~~ data under different *RH* conditions. The range of values shows the difference between the modeled data and *NEq.* ~~parameterized equatio~~data at different Cu^{2+} concentration. At low *RH* and consequently relatively low ALWC, γ_{HO_2} is more sensitive to $[Cu^{2+}]$ ~~expecially~~especially at low $[Cu^{2+}$~~] (<10^{-4}M).~~$^{+}$]. This sensitivity ~~can not~~cannot 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} 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,~~-1 molar concentration~~M~~, and a relative humidity between 40~~%~~~~%-90%, the *NEq.*~~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.~~. Beyond the range, the application of the ~~NovEquation~~*NEq.* may cause a large deviation. The HO_2 uptake under dry conditions needs further investigation in the future, but probably it 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 uptake may then be neglected for typical tropospheric conditions (Taketani et al., 2008; Kanaya et al., 2009; Taketani and Kanaya, 2010; Thornton et al., 2008; 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 MARK modeled γ_{HO_2} ~~and~~to the corresponding calculated values from the ~~new parameterized equation. log$_{10}$~~NEq~~-~~. ~~(15~~$log_{10}($~~γ_{mod}~~$\gamma_{mod})$ is the logarithmic value of modeled γ_{HO_2} and ~~log$_{10}$~~$log_{10}($~~γ_{cal}~~$\gamma_{cal})$ is the calculated value from the ~~new parameterized equation.~~NEq. ~~(15).~~

3.~~4 Impact~~5 Evaluation of the impact of the new HO$_2$ uptake ~~evaluated with the novel parameterized equation~~parametrization in the Wangdu campaign

Many model studies (Lakey et al., 2015; Mao et al., 2013b; Martinez et al., 2003; Tie et al., 2001; Whalley et al., 2015) suggest that heterogeneous uptake of HO$_2$ radical affects the global distribution of trace gases and the atmospher~~e~~ic 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 (Li et al., 2019b; Lou et al., 2014). The competition of HO$_2$ 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~~, HO$_2$ uptake~~ (Tan et al., 2020), the HO$_2$ uptake coefficient and the ratios of the HO$_2$ uptake loss rates ($TR_{HO2uptake}$) to the sum of the ROx termination rates ($TR_{ROxsinks}$) are calculated with direct measurements of the ROx radicals, trace gas ~~compounds~~species, ALWC and the aerosol ~~properties.~~condensed phase component concentrations (please see the SI for details). The experimental determined ROx termination rates include reaction channels from OH + NO$_2$~~ /~~, OH + NO, HO$_2$ + 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~~5.1 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 it is a regional site. The observation~~ was~~s were~~as~~ carried out in 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 relative humidity, the Wangdu area is a high-temperature and high-humidity ~~stage~~environment with a monsoon climate.

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 /℃	27±4	±0.05%
Pressure /hPa	1000±5	±0.05%

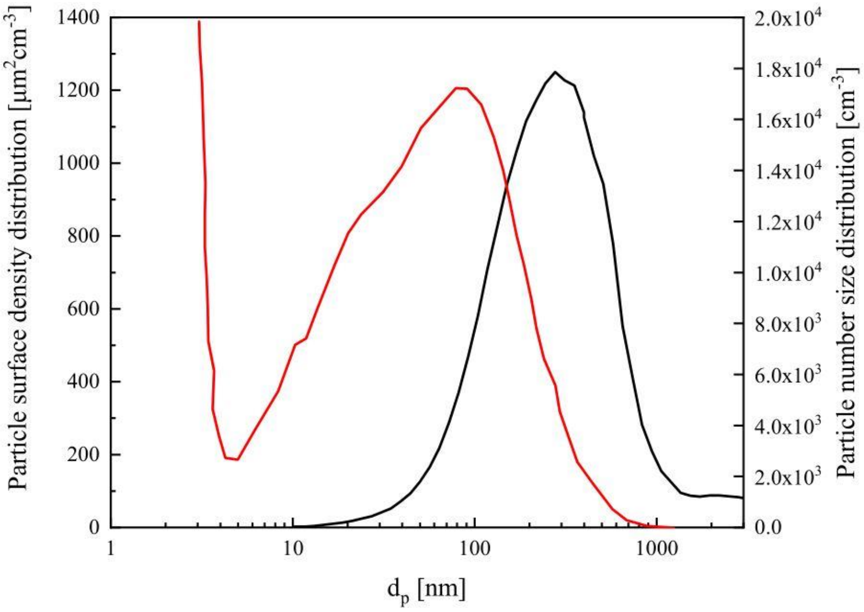
RH/%	~~58~~61±18	±0.05%
O_3/ppb	55.6±9.0	±5%
NO_x/ppb	10±13.6	±20%
HONO/ppb	0.8±0.24	±20%
CO/ppm	0.6±0.19	<5%
Isoprene/ppb	0.5±0.11	±15%-20%
HCHO/ppb	7±0.69	±5%

3.~~4~~5.2 Calculation of ~~aerosol liquid water content (ALWC) in Wangdu campaign~~

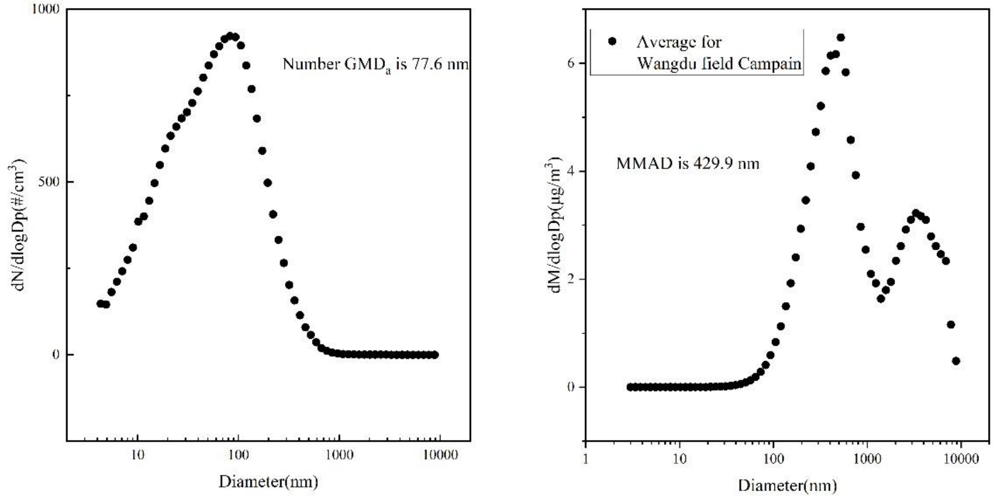
~~Assuming aerosol particles are all spherical, particle total surface area (S) can be calculated as:~~

~~$S = \int \frac{dN}{d\log D_p} \cdot \pi D_p^2 \cdot d\log D_p$ (18)~~

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



~~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%.~~

~~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-Kőhler 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$\left(D_p, RH\right)$ 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:~~

~~$\mathrm{ALWC} = \left[\frac{\pi}{6}\sum_i N_i D_{p,i}^3 \left(g\left(D_p, RH\right)^3 - 1\right)\right]\rho_w$ (19)~~

~~Where N_i represents the number concentration of dry particles of the ith bin, $D_{p,i}$ 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 2.5μm, 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 2.5μm) 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. For particle radius smaller than 2.5μm, which are the most contributing bins of aerosols in HO_2 uptake, the mass fraction of Cu is about 33%−100% compared with other two size bins in ambient aerosols (2.5-10 μm, >10μm) (Mao et al., 2013a). According to previous research results, the dissolution ratio of copper in aerosol particles varies from 20% to 70% in different regions, being solubility lower in smaller particles (Fang et al., 2017; Hsu et al., 2004; Hsu et al., 2010b). Therefore, when using the *NEq.* ~~empirical paraterization equation (Eq.15)~~ to calculate the HO_2 heterogeneous uptake coefficient, it is necessary to reduce the copper concentration 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~~The hourly resolution total copper concentration (ng m^{-3}) is divided by the aerosol volume concentration ~~the hourly resolution total copper concentration (ng m^{-3})~~ and the atomic mass of copper (64) to obtain the total copper ~~molarity~~molar concentration in the aerosol (mol L^{-1}). γ_{HO_2} = ~~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. According to the research results, it is found that the dissolution ratio of copper in aerosol particles from 40% to 60% in different regions~~ rather depends on copper concentration so we also evaluate the influence of copper solubility on the uptake coefficient. What is~~'s~~ more, the unequally distribution of copper ions will also influence the HO_2 uptake coefficient (details in the SI).

~~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 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). The aerosol liquid water content is divided by hourly resolution total copper concentration(ng m^{-3}) and the atomic mass of copper (64) to obtain the total copper molality in the aerosol (mol L^{-1} H_2O). 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~~5.3 γ_{HO_2} estimated at Wangdu field campaign

By inputting the soluble copper concentration, aerosol mass concentration, aerosol particle geomet~~e~~ric mean diameter and the corresponding relative humidity and temperature into the *NEq.* ~~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 1 hour.~~is 1 hour. The aerosol pH is calculated using the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) and the averaged value is 3.41± 0.69 (1σ). 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 of~~ The results of a fit to a Gaussian~~Amp~~ function results in a γ_{HO_2} ~~is~~ value of 0.~~109±0.005~~ 116 ± 0.~~045~~ 086 (1σ) ~~in daytime and 0.1390±0.007053 at night in~~ the Wangdu campaign~~.~~ (γ_{HO_2} will increase ~~1.57 times~~ from 0.~~075~~065±0.~~031~~ 051 (1σ) at 10% solubility to 0.~~193~~196±0.~~079~~ 142 (1σ) at 70% solubility for the summary of day and night data).

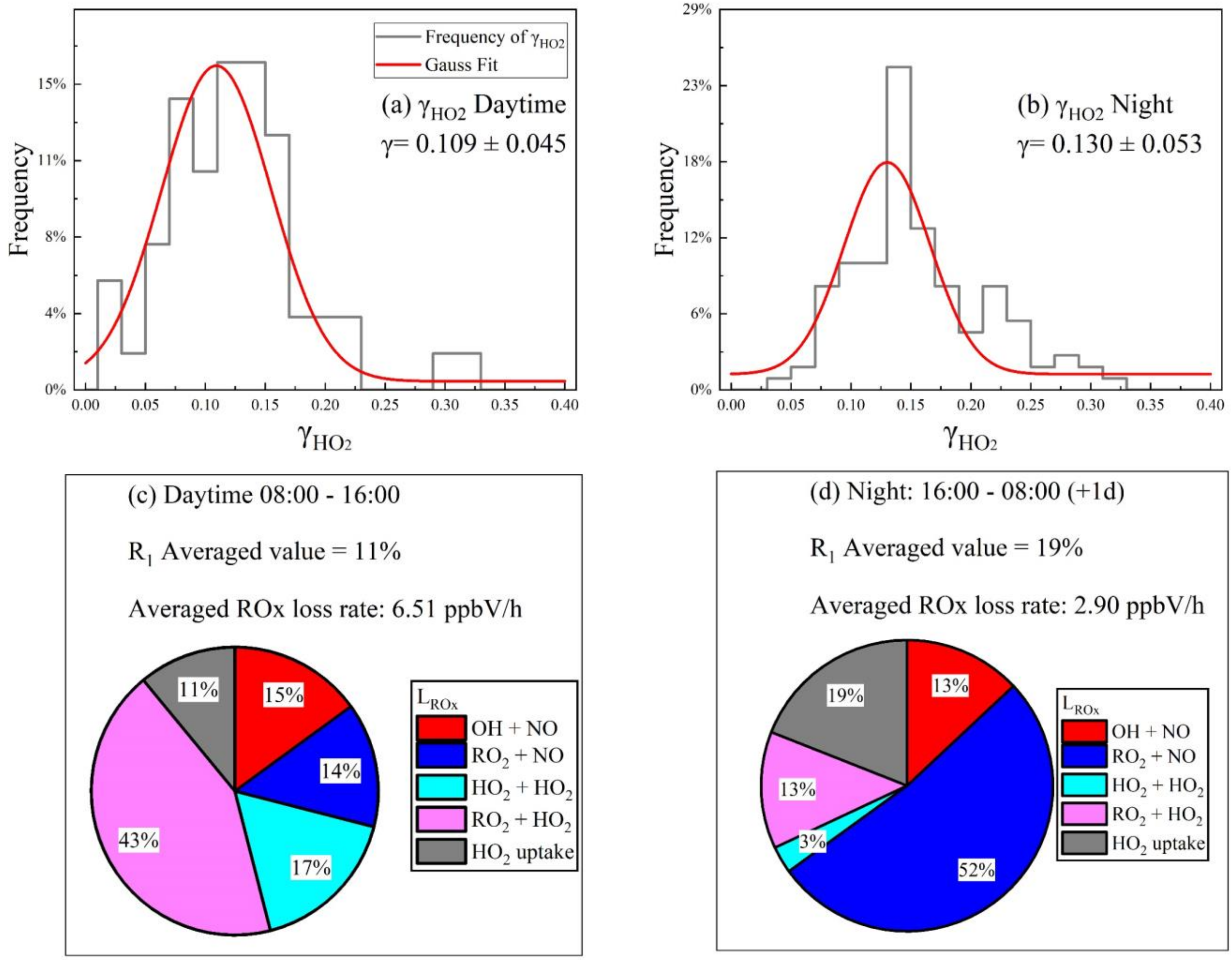
~~These values are likely the maximum possible upper limit of γ_{HO_2} for near-ground layer aerosols. Because of the distribution of TMI is mainly in the accumulation and coarse mode of aerosol, with the height increasing, the amount of copper in the aerosol decreases, leading to a decrease in the heterogeneous 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 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 HO_2 heterogeneous uptake coefficient in this campaign. The interaction between organics and soluble copper and the influence of organics on aerosol properties will lead to further uncertainty of uptake coefficient. Lakey et al.~~(Lakey et al., 2016b; Lakey et al., 2015; Lakey et al., 2016c) ~~have also shown that the addition of a organic compound to Cu(II) doped aerosols, such as oxalic acid which forms oxalate ions $(C_2O_4)^{2-}$ in the aerosol, results in lower γ_{HO_2}.~~ 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 (1σ). This value is ~~similar~~ in the range of ~~to~~ our estimation in this paper considering the influence of aerosol morphology and 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 (22~~0~~) and (23~~1~~).

$$L_{HO2\text{uptake}} = 0.25\cdot v_{HO_2}\cdot[ASA]\cdot[HO_2]$$ (22~~0~~)

$$R_1 = \frac{L_{HO2uptake}}{L_{ROx}}$$ (23~~1~~)

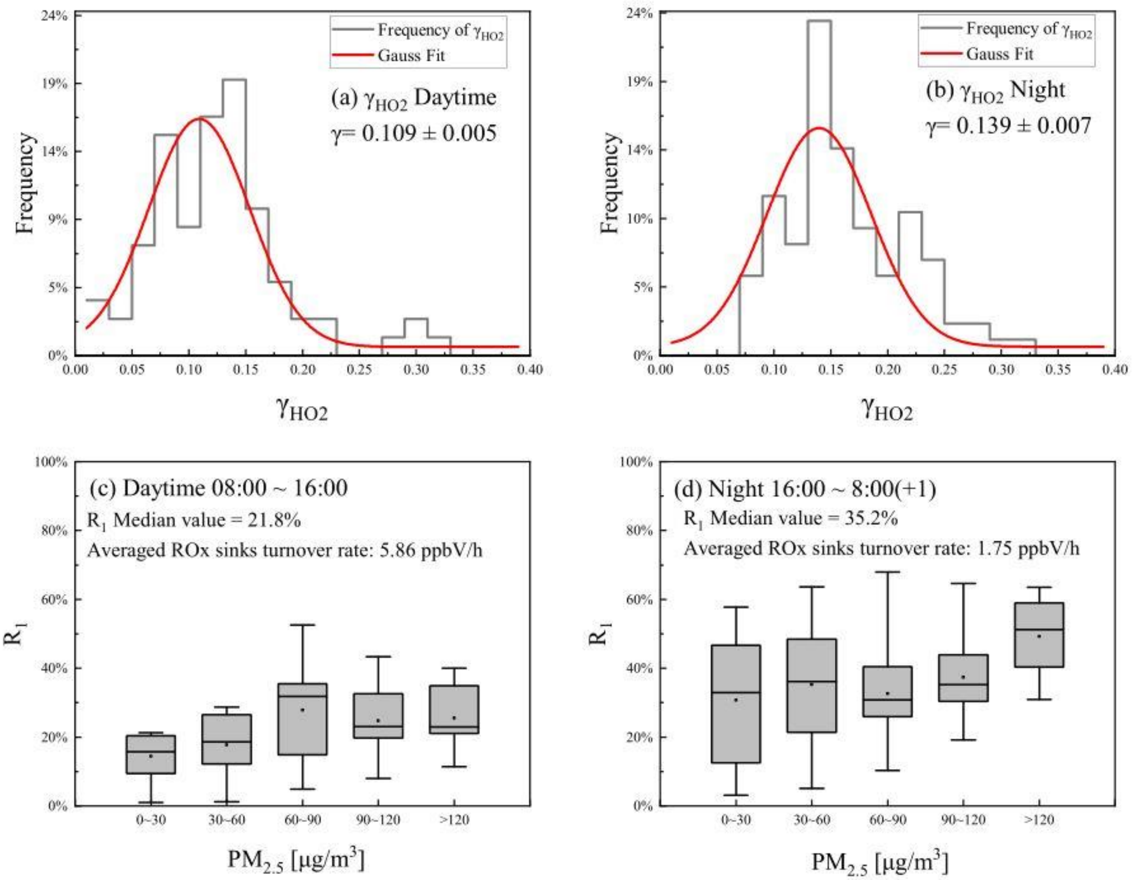
$[ASA]$ is the aerosol surface area [$\mu m^2\ cm^{-3}$].



~~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) and re-aerosolize 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 HO_2 uptake coefficient. Li et. al(Li et al., 2019b) find that the rapid decrease of $PM_{2.5}$ in China will slow down the reactive uptake rate of HO_2 radicals by aerosol particles may be a very important and pervasive factor for the increase in ozone in the North China Plain. They take γ_{HO_2} as 0.2 in their model calculation. However, the results of the MARK model and empirical equation calculations in this paper suggest that HO_2 uptake coefficient is in general smaller and highly variable. Thus further research is needed to study the effects of heterogeneous uptake of HO_2 on gas phase and heterogeneous~~

~~physicochemical reactions under different environmental conditions in different regions and when the variability of γ_{HO_2} is considered..~~



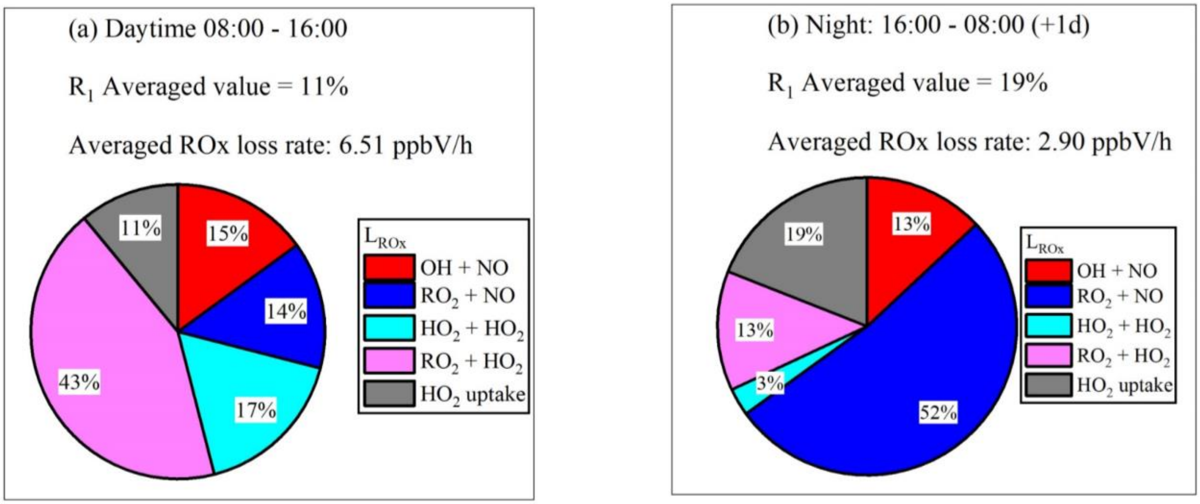


Figure ~~6~~4: ~~Daytime and night values of the HO_2 uptake coefficient (γ_{HO_2}) and~~ R_1 calculated ~~based on~~by the ~~new empirical equation.~~*NEq.* ~~(Equation 15).~~ ~~A Gaussian distribution (red line) is fitted to γ_{HO_2} frequency distribution in panelof γ_{HO_2} (a) and (b),) yielding a mean uptake coefficient of 0.109 with a standard error of 0.0045 in daytime and 0.1390 with 0.007053 at night. Box plot...~~ Pie charts show the values 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 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~~ loss rates ~~include reaction channels from OH + NO_2 / NO, HO_2 + HO_2, HO_2 + RO_2, RO_2 + NO. Considering the solubility~~for ROx during daytime (~~c~~a) and ~~size distribution of aerosol 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.~~

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

~~$R_1 = \frac{TR_{HO2uptake}}{TR_{HOxsinks}}$ (21)~~nighttime (~~d~~b). The averaged

~~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~~loss rate is 6.5~~.9~~ ppbV/h and that for nighttime (16:00~~~~~ −08:00 (+1d)) is ~~1.7~~2.9 ppbV/h.

~~In Fig. (4 a and b), no~~ No ~~significiant~~significant difference of γ_{HO_2} is observed during daytime and night. ~~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%~~
~~NO_2~~	~~±20%~~

~~Indirect measurement uncertainty is calculated from the direct measurement according to a certain mathematical formula. In this way, the uncertainty of the direct measurement quantity will inevitably affect the indirect measurement quantity, and the magnitude of this influence can also be calculated by the corresponding mathematical formula which is called the uncertainty propagation equation.~~

~~$N = F(x, y, z, \ldots)$ (21)~~

~~$u_{r\_meas} = \frac{u_N}{\bar{N}} = \sqrt{(\frac{\partial \ln F}{\partial x})^2 (u_x)^2 + (\frac{\partial \ln F}{\partial y})^2 (u_y)^2 + (\frac{\partial \ln F}{\partial z})^2 (u_z)^2 + \cdots}$ (22)~~

~~Where N is the indirect measurement quantity. u_{r_meas} is the relative combined standard uncertainty of the indirect measurements used as model constraints. x, y, z and other direct measurement quantities are independent physical quantities refer to RH, copper concentration... The corresponding relative combined uncertainties are u_x, u_y, u_z... They inevitably affect the indirect measurement, so that the N value also has a corresponding uncertainty u. Since the uncertainty is a small amount, which is equivalent to the "increment" in mathematics, the calculation formula of the uncertainty of indirect measurement is basically the same as the total differential equation in mathematics.~~

The HO_2 uptake coefficient is slightly higher at night due to the higher *RH* (57.6% at day and 67.4% at night). However, because of the high uncertainty of the uptake coefficient, such a high trend cannot be concluded to other cases. HO_2 heterogeneous uptake reactions with aerosol particles have small impact on ROx radical termination at daytime as shown in Fig. (4 ~~c~~a). However, HO_2 uptake may be important in the termination of ROx radicals at night shown in Fig. (4 ~~d~~b). The daytime ratio R_1 is lower than it is at night because of the lack of photochemical reactions, thus a longer HO_2 lifetime at night. The high proportion of RO_2+NO during night is due to high [NO] at dawn.

The RO_2 concentration is also important when evaluating the impact of HO_2 uptake. Using the modeled value of RO_2 concentration in Wangdu campaign, a higher proportion of HO_2 uptake to about 21% of ROx sinks in daytime can be calculated.

However, using the modified field measured RO_2 concentration in Wangdu campaign, HO_2 uptake is less important in the budget of ROx as shown in Fig (4 ~~c~~aa), which is in line with the results from Tan et al. (2020).

3.5.4 Discussion of uncertainties of γ_{HO_2} estimated at Wangdu field campaign

The impact of HO_2 aerosol uptake on the ROx budget is complicated by large uncertainties in the HO_2 uptake coefficient under ambient conditions. The *NEq.* 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 deviations for larger particles.

Organic content of an aerosol particle may affect several important parameters in the uptake model (Lakey et al., 2016c; Lakey et al., 2015). 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 matter would change the value of γ_{HO_2}.We tested the core-shell morphology of aerosol particles influence on HO_2 uptake in the Wangdu campaign (details in the SI). Organic matter will lower the uptake coefficient about 25% to 40% under the assumption of 20%-50% $PM_{2.5}$ mass is organic matter.

Another uncertainty comes from aerosol particles morphology. 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). 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 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}. Anyway, aerosol particles morphology relative to an aqueous phase will influence the uptake coefficient of HO_2. The uptake process would vary with mixing state of the particles, thus the predicted γ_{HO_2} values here may be biased as a ~~result, but~~result but represents an average over bulk aerosols.

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., 2016b; Lakey et al., 2015; Lakey et al., 2016c) have also shown that the addition of an organic compound to 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.

As noted above, the value (0.116 ± 0.086 (1σ)) estimated by the *NEq.* represents the upper limitation of γ_{HO_2} in the Wangdu field campaign.

4 Summary and conclusions

~~The impact of HO_2 aerosol uptake on the ROx budget is complicated by large uncertainties in the HO_2 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 HO_2 concentration gradients within the aerosol particle condensed phase also cause 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 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., 2016b; Lakey et al., 2015; Lakey et al., 2016c) ~~have also shown that the addition of an organic compound to 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.~~

Taketani et al. collected the filter samples of aerosol in Mts. Tai and Mts. Mang, North China (Taketani et al., 2012) and re-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. ~~The impact of HO_2 uptake on ROx budget is complicated with great uncertainties at the ambient conditions (the combined standard uncertainty of γ_{HO_2} is ±40.7%, of $TR_{HO2uptake}$ is ±43.7%, of R_1 is ±59.4%.). A fixed value of~~ Li et. al (Li et al., 2019b) suggest that the rapid decrease of $PM_{2.5}$ in China has slowed down the reactive uptake rate of HO_2 radicals by aerosol particles and could have been the main reason for the increase in ozone in the North China Plain in the recent years. They apply a value of the uptake ~~coeffient~~coefficient of ~~of~~ 0.2 in their model calculations. However, the results of the MARK model and of the *NEq.* ~~empirical equation~~ in this paper suggest that the HO_2 uptake coefficient could be smaller and highly variable 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 physico-chemical reactions under different environmental conditions in different regions.

The ~~new~~ novel parameterized equation proposed in this paper provides an effective way for more detailed calculation of the effects of HO_2 heterogeneous reactions on the atmospheric radical budget, ozone production and particulate matter generation. This is the first attempt to parameterize the heterogeneous uptake coefficient of HO_2 with aerosol particles in China campaign. This equation estimates the γ_{HO_2} in a comprehensive field campaign which is in agreement with the simulation results from the comparison of gas phase radical concentrations (Tan et al., 2020). 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, organic content, as well as the aerosol liquid water should be added for future field campaigns for the study of the HOx radical budget.γ_{HO_2}

Appendix A

Table A1 Description and units of parameters used in the MARK model and the parameterized equations

Parameter	Description	Unit
	Used in the parameterized equation	
γ_{HO_2}	HO_2 uptake coefficient	-
α_{HO_2}	Mass accommodation coefficient of HO_2 which is the probability that a HO_2 molecule colliding with the aerosol surface leads to dissolution, reaction or volatilization	-
υ_{HO_2}	Mean molecular speed of HO_2	$cm\ s^{-1}$
R_d	Count Median Radius of the aerosols	cm
R_c	radius of the aqueous core	cm
H_{corr}	Henry's constant corrected for solution pH $H_{corr} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right)$	$mol\ cm^{-3}\ atm^{-1}$
H_0	physical Henry's law constant	$mol\ cm^{-3}\ atm^{-1}$
H^{cc}	effective Henry's law constant	$mol\ cm^{-3}\ atm^{-1}$
H_{org}	Henry's law constant of HO_2 for organic coating	$mol\ cm^{-3}\ atm^{-1}$
R	gas constant	$cm^3\ atm\ K^{-1}\ mol^{-1}$
T	temperature	K
RH	relative humidity ranging from 0.4 to 0.9	0-1
ALWC	aerosol liquid water content	$g\ cm^{-3}$

[PM]	Mass concentration of $PM_{2.5}$	$\mu g\ cm^{-3}$
D_g	gas phase diffusion coefficient of HO_2	$cm^2 s^{-1}$
D_{aq}	aqueous phase diffusion coefficient	$cm^2 s^{-1}$
D_{org}	solubility and diffusivity of HO_2 in the organic coating	$cm^2 s^{-1}$
ε	ratio of the radius of the aqueous core (R_c) and the particle (R_d).	-
l	Thickness of organic coating which is calculated from the volume ratio of the inorganics to total particle volume with the assumption of a hydrophobic organic coating (density, 1.27 g cm^{-3}) on the aqueous inorganic core (with a density of 1.77 g cm^{-3}).	cm
Used in the corrections in the MARK model or the classical parameterized equation		
ρ	density of the aerosol particles	$g\ cm^{-3}$
I	Solution molar ionic strength	M
A	activity coefficient for gas phase HO_2 and other neutral small molecules	-
φ_x	activity coefficient of ion in solution	-
m_y	molality of an ion in solution	M
$\varepsilon(x, y, I)$	"interaction coefficients", the summation extends over all ions (y) in the solution at a molality of m_y	-
$[x_i]_{equ}$	effective molality of an ion x_i	M
$[\overline{HO_2}]$	averaged steady-state HO_2 concentration over the volume of the particle	M
$[HO_{2(r)}]$	HO_2 concentration at the surface of particles	M
K_{eq}	solution equilibrium constant for HO_2 in the gas phase	$M^{-1} s^{-1}$
k_{eff}	comprehensive liquid phase reaction rate coefficient which encompasses both HO_2 dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO_2 uptake process	$M^{-1} s^{-1}$
k_{TMI}	second order rate coefficient (k_{TMI}) of HO_2 and O_2^- with transition metal ions used in the classical equation	$M^{-1} s^{-1}$
k^1	effective rate coefficient used in the classical equation proposed by IUPAC	$M^{-1} s^{-1}$

~~-used in models may cause errors when evaluating the atmospheric oxidant capacity. The new parameterized equation in this paper provides a novel way for more detailed calculation of the effects of HO_2 heterogeneous reactions on atmospheric radical budget, ozone production and particulate matter generation. In addition, many model calculations suggest that other soluble TMIs, including Fe(II)/Fe(III) and Mn(II)/Mn(III), play a similar role in cloud droplets~~(Graedel and Weschler, 1981; Graedel et al., 1986)~~. The Cu-Fe and Fe-Mn redox coupling mechanism in clouds requires further research. In ambient aerosol, Fe concentration is about 10~100 times(Mao et al., 2013a) higher than that of Cu, and 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. 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.~~

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 María-Teresa Baeza-Romero contributed the laboratory studies of HO_2 uptake ~~coefficients~~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 available upon request for the corresponding author (k.lu@pku.edu.cn).

Acknowledgments

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