

Response to the comments of reviewer #4

This review covers the 2nd revised version of the manuscript ACP-0218

“Influence of aerosol copper on HO₂ uptake: A novel parameterized equation” by Huang et al

5 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.

The first author of this manuscript is Huan Song, not Huang.

10 This manuscript reports an explicit model of uptake of HO₂ radicals to deliquesced inorganic aerosol particles to partially reconcile previous inconsistencies among experimental measurements and parameterizations. This includes a detailed treatment of the aqueous phase chemistry of HO₂ and superoxide with Cu ions, as well as considering effects of Setchenov salting and ionic strength. The model is also used to interpret data from a field campaign. The previous review rounds already covered the general aspects regarding scientific relevance and significance the topic, which are undoubted. In response to
15 previous comments related to a dataset also included to fit a parameterization, the authors of that dataset have joined the revised version of the paper and this version now includes an updated description of experimental details and revised data analysis related to that dataset. In response to another review, the authors have expanded the model description and the discussion related to sensitivity and uncertainty. Overall, this work provides valuable new information, especially the fact that taking into account the properties of the concentrated solutions of deliquesced aerosol particles allows to calculate HO₂ uptake coefficients
20 using known and well documented aqueous peroxy radical chemistry involving Cu ions. While the model includes some complexity by involving links to nitrogen oxides and sulfur, it lacks inclusion of the interaction with the Fe(II)/Fe(III) redox couple, which usually is associated with the presence of Cu in atmospheric particles and may have important impacts. Nevertheless, the manuscript provides progress in understanding uptake of HO₂ to aerosol particles.

25 In spite of this being the 2nd revised version of this manuscript, still a number of deficiencies exist that should be addressed. In the comment below, I list the line numbers of the pdf file of the revised manuscript version. In principle, these concerns are rather minor in character, but still numerous. They should be addressed before the manuscript may be accepted for ACP.

1) Language: the new text additions are sometimes misleading, mostly due to deficiencies in the English language. This should
30 be fixed by a thorough work-through by the authors.

2) Abstract line 24: the IUPAC website provides a recommendation for a number of different deliquesced aerosol systems, not only cloud droplets. See also comment further below on the same aspect in the manuscript.

We made the modifications to this aspect in the manuscript. In the abstract line 24, we deleted “for cloud droplets”. On line 253, we change the words to “deliquesced aerosol particles” and on line 262, we added the words “proposed for HO₂ uptake for deliquesced aerosol particles” as recommended by the (24) opinion.

And the classical parameterized equation was confirmed by researches of reactive gas molecular uptake on dilute solution droplets (Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002; Hu et al., 1995).

3) Line 26: not sure whether it is useful to have the parameterization in the abstract without explanation of symbols.

40 We added an instruction in the double brace in the abstract saying the explanations for the symbols are in the Appendix.

4) Line 27: The Wangdu campaign is not something the reader understands without introduction. Either explain in more detail, ‘data from a campaign in the Wangdu region’, or just ‘data from a field campaign’.

We deleted the name of the field campaign on line 27.

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5) Lines 42-45: these sentences should be split up, and the reason for the lower reactivity in absence of transition metals should be explained, including the self reaction of HO₂ that has been parameterized by Thornton et al. In addition, a language issue here: The impact of HO₂ uptake is not depending on a parameterization. It is the model output, or the calculated response of some parameters to HO₂ uptake that changes. This is different.

50 We changed this part as:

“The model results of HO₂ uptake influence is lowered when a parameterized equation of γ_{HO_2} is used without considering the influence of transition metal ions (TMIs) (Thornton et al., 2008). The reasons for the lower reactivity in absence of TMI including the lower reaction rate of aqueous HO₂/O₂⁻ reactions(Thornton et al., 2008). However, in spite of the lower HO₂ uptake coefficient used a significant impact on the calculated [OH] and O₃ production rate are suggested for air masses over Chinese megacity areas (Macintyre and Evans, 2011).”

6) Line 73: symbols used in eq. (1) and (2) need to be explained

We added an instruction in the first of the paragraph saying the explanations for the symbols are in the Appendix.

60 7) Same paragraph: it does not become clear enough how the uptake coefficient was retrieved from the model output. This should be briefly described here.

We changed the sentences on line 73 as:

“The model directly calculates the averaged quasi-first order gas phase HO₂ uptake loss rate at steady state, $k_{net}(s^{-1})$, in Eq. (1). γ_{HO_2} is retrieved by Eq.(2) considering the influence of aerosol liquid water content (ALWC) [g cm⁻³] rather than surface density because of the influence of the RH on the uptake process (Kuang et al., 2018; Bian et al., 2014).”

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8) Line 106: some numbers should be given here. What is the ratio between H^{cc} and H_0 over the RH range considered in this study? Same sentence: why does H^{cc} depend strongly on the Cu concentration? The dominant solute is ammonium sulfate, which should be the main driver of salting and ionic strength, isn't it.

We gave the ratio of H^{cc} to H_0 of HO_2 in the revised MS as follows on the line 106:

“According to this correction, H^{cc} of HO_2 increases with RH. The ratio of H^{cc} to H_0 ranges from 0.03 (40% RH, $I=16.7$) to 0.34 (80% RH, $I=5.5$). Although the salting effect and the ionic strength are mainly driven by $[NH_4^+]$ and $[SO_4^{2-}]$, ionic strength increases quickly from 5.9 to 9.5 with $[Cu^{2+}]$ from 0.1 M to 1 M and limits the solubility of HO_2 gas molecules.”

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9) Line 115: Two things here: the solubility of Fe is not a defined quantity, the authors may refer to the solubility of Fe-containing minerals. There are literature reports about what fraction of Fe is typically in dissolved form. In addition, there is a language issue here (many similar cases throughout the manuscript), the sentence reads like the solubility of Fe is related to its ratio to Cu, which is certainly not true.

80 10) Line 118: Neglecting the presence of Fe should lead to a stronger caveat for this work. The authors cite the Mao et al. (2013) work a few times, which clearly indicates a strong impact of the Cu/Fe ratio on the fate of HO_2 products in the aqueous phase. Fe may reduce the contribution of recycling of peroxy radicals to lower the effective HO_2 loss rate, and Fe might be relevant for the interpretation of the effect of HO_2 uptake on the HOx budget in conjunction with the field data.

85 There is no direct evidence of the impact of the Cu/Fe ratio on the fate of HO_2 products as proposed by Mao, so in this MS we used the model mechanisms for HO_2 uptake to produce H_2O as many other papers (Mozurkewich et al., 1987; Hanson et al., 1992; Thornton and Abbatt, 2005; Thornton et al., 2008; Taketani et al., 2009; Macintyre and Evans, 2011). On line 118, we change this part as:

90 “Since there is no direct evidence of the existence of Cu/Fe redox reactions of HO_2 which produce H_2O rather than H_2O_2 as proposed by (Mao et al., 2013), in the scope of this paper, HO_2 uptake produce H_2O separately by Cu and Fe free ions as proposed by many researches (Mozurkewich et al., 1987; Hanson et al., 1992; Thornton and Abbatt, 2005; Thornton et al., 2008; Taketani et al., 2009; Macintyre and Evans, 2011) and the mechanism summarized by IUPAC. Fe free ions can be seen as the equivalent Cu free ions in the application of the MARK model or the parameterized equation mentioned below.”

11) Line 135: in eq. (10) and (11), the subscript ‘equ’ is misleading, since it should refer to ‘effective’ and not ‘equilibrium’ or ‘equation’. So ‘eff’ would be better.

We changed ‘equ’ to ‘eff’ in this part and updated the meaning of $[Cu^{2+}]_{eff}$ which is now the sum of effective copper concentration and other TMI equivalent copper concentrations.

12) Line 148: this paragraph is not sufficiently clear. k_{eff} seems to be the apparent first order loss rate coefficient of HO_2 in the aqueous phase (not involving solubility). Typical numbers should be provided; otherwise it would not be understandable,

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why a 1 M Cu(II) solution would not lead to a very short reacto-diffusive length and thus strong concentration gradients in HO₂. Also the reasons for the apparently low values should be explained, as this must result from complex recycling occurring, since the first reaction of Cu(II) with HO₂ is very fast.

105 k_{eff} is the comprehensive liquid phase reaction rate coefficient which encompasses both HO₂ dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO₂ uptake process. It is calculated by Eq.19 and include the influence of the salting out effect of HO₂. Typical value is about $2.9 \times 10^6 \text{ M s}^{-1}$ with 1 M Cu²⁺ and $3.25 \times 10^4 \text{ M s}^{-1}$ with 0.001M Cu²⁺. k_{eff} will change dramatically according to the concentration of equivalent copper ions and the diameter of particles.

We changed the relevant sentences and recalculated the ratio considering the high copper concentration on line 148 and following part:

110 “and D_{aq} is the aqueous phase diffusion coefficient [cm^2s^{-1}], k_{eff} is the comprehensive liquid phase reaction rate coefficient which encompasses both HO₂ dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO₂ uptake process. k_{eff} is calculated by Eq.19 and includes the influence of the salting out effect of HO₂ and the ionic strength effects on TMI. k_{eff} will change dramatically according to the concentration of equivalent copper ions and the diameter of particles. Higher Cu concentration will make the ratio smaller and cause larger uncertainties, however, in the copper-doped
115 aerosol particle, because of the high value of k_{eff} (typical value is $2.9 \times 10^6 \text{ M s}^{-1}$ with 1 M Cu²⁺ and $3.25 \times 10^4 \text{ M s}^{-1}$ with 0.001 M Cu²⁺) and small Count Median Diameter (R_d) (usually smaller than 1 μm), the ratio $\frac{[HO_2]}{[HO_2(r)]}$ is close to 1. At a diameter of 100nm, and a relative humidity between 40% and 90%, the condensed phase copper ion concentration varies from 10^{-5} to 1 M, the average ratio of the surface HO₂ concentration and the condensed phase HO₂ concentration is beyond 0.87 at every Cu concentration. The ratios are calculated by simulation of k_{eff} and the accordingly calculations by Equation (12) and (13).
120 Thus, in this model, we assume the surface concentration of HO₂ equals to the condensed phase average HO₂ concentration.”

13) Line 158: the value of the accommodation coefficient is not related to the amount of Cu. The amount of Cu may control the uptake regime, with large amounts leading to uptake becoming accommodation limited. But the value of alpha is independent of Cu, unless it is involved in the process of surface to bulk transfer of HO₂. Are the authors confusing
125 accommodation coefficient with uptake coefficient? Also Table 1 is misleading, as the data in column seem to be uptake coefficient, as indicated in the Table caption, but inconsistent with the column header.

14) Line 162: probably related to the previous, the high accommodation coefficient for HO₂ does not automatically mean it has a high loss rate. It only means that gamma may get large, if a strong sink is available in the condensed phase.

15) Line 164: language: The MARK model probably does not make the selection of alpha, but the authors selected it.

130 16) Line 167: as mentioned before, please clarify the column header of the table and the caption (alpha or gamma)

The accommodation coefficient is surely not influenced by the concentration of Cu ions if the viscosity of particles maintains. While the accurate accommodation coefficient can be only measured with no limitation of aqueous mass transfer flux in which

situation, a high aqueous reaction rate. We changed this part in section 2.3 to avoid misleading. We also changed the column header.

135 “The accommodation coefficient of HO₂ (α_{HO_2}) is independent of the concentrations of free Cu ions if the viscosity of particles maintains. While the more accurate accommodation coefficient can be only measured with no limitation of aqueous mass transfer flux, in which situation, α_{HO_2} equals to γ_{HO_2} . HO₂ uptake coefficients are summarized for copper-doped inorganic aerosol particles from various previous laboratory studies. The uptake coefficient of HO₂ is approximately 0.5 in sulfate aerosol and even higher for chlorine or nitrate aerosol because of the catalytic effect of Cu²⁺ on aqueous HO₂/O₂⁻ (Table 1). In this
140 situation, the aqueous reactions are fast enough for the uptake process be limited primarily by the mass transport process (accommodation) and the uptake coefficient equals to the accommodation coefficient. Thus, the MARK model typically uses α_{HO_2} as 0.5. We also tested the influence of the accommodation coefficient on calculated HO₂ uptake coefficient in a field campaign, details please see the Supplementary Information.”

145 17) Line 172: first sentence: language!
We changed the word as “included”.

18) Line 178: SMPS = Scanning Mobility Particle Sizer or Scanning Mobility Particle Spectrometer

19) Line 179: aerosol particles were produced using a ...

150 We changed this part as:

“...and the total aerosol surface area was determined with a Scanning Mobility Particle Sizer (SMPS) at the end of the flow tube. Aerosol particles were produced using a constant output atomizer...”

20) Line 198 and following: while the model is indeed used to explore the RH dependence of HO₂ uptake and associated
155 aqueous phase chemistry, the comparison to experimental data is not really covering a substantial RH range. So that is essentially limited to the effect of the Cu(II) concentration.

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. 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 dependence, the change of the
160 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, HO₂ and H₂O₂. The MARK model was presented to simulate the change of the uptake coefficient with RH in Figure 1.

21) Line 230: HO₂ uptake at low Cu content: the figure should be plotted in log y-scale to demonstrate that the remaining
165 uptake at low Cu content is driven by self reaction of HO₂ (should be second order in HO₂).

The aim of this MS is to explore the influence of TMI and RH on HO₂ uptake rather than HO₂ aqueous self-reaction mechanism. For this reason, we believe Figure 2 is better now to demonstrate the trend of HO₂ uptake coefficient under different copper ions gradient.

170 22) Line 231: What does the sentence ‘The threshold is also consist in ...’ mean? What are droplets?

On line 231 the word should be ‘consistent’ and the droplets refer to cloud or rain droplets.

23) Line 233: I understand that increasing Cu content drives uptake to the accommodation limit; but why should that be determined by the solubility?

175 We changed the last sentence in the paragraph: “As the copper concentration increasing, the solution ionic strength increases and γ_{HO_2} rapidly rises to the limit of the accommodation coefficient and the limitation of the HO₂ solubility.”

24) Line 254: the Thornton et al. (2008) parameterization was developed for deliquesced aerosol particles, not cloud droplets. This repetitively comes up below again.

180 25) Line 262 and following: as mentioned above, the Thornton et al. and IUPAC recommendation has not been suggested for dilute aqueous droplets but actually for deliquesced aerosol particles. As discussed in Thornton et al. but also in the comments accompanying the IUPAC recommendations, the fact that k_{TMI} is lower than the actual known rate coefficient of HO₂ or O₂⁻ with Cu(II), is assumed to likely result from the combined effects of solute strength effects. It is indeed the added value of this work to make this aspect more quantitative. The authors could emphasize this somewhat more to detail the individual
185 contributions of Setchenov salting, of ionic strength and of the recycling efficiency among the copper and peroxy species to the reduction of the effective rate coefficient. The advantage of eq 15 is that it correctly represents the transition between the reacto-diffusive regime (when k_{eff} is higher) to the homogeneous bulk reaction regime covered by the parameterization suggested in this work (eqs 18-21)

190 Corrections about the word “droplets” to “deliquesced aerosol particles” are done in the revised MS mentions in the response to opinion (2).

We deleted the discussion of the rate constant of Cu²⁺ with HO₂/O₂⁻ and added the sentence:

“The low reaction rates used here in the *CEq.* are assumed to likely result from the combined effects of solute strength effects as discussed by Lakey et al. (2016).”

The individual contributions are mentioned in the last paragraph of Section 3.3 as:

195 “The MARK model uses the same framework with the *CEq* and considers the Setchenov salting out and ionic strength effects on HO₂ uptake more comprehensively and detailly and proposes k_{eff} as the effective reaction coefficient (Eq.19). 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 [Cu²⁺] and *RH* on γ_{HO_2} .”

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26) Line 310 and following: the authors should clearly state that this parameterization is only reasonable as long k_{eff} remains sufficiently small, such that no HO₂ gradients within particles develop. While they seem to show that this is valid with the mechanism involving Cu only, it is not granted that this is still true when for instance including Fe ions in the mechanism which could lead to an increasing sink for HO₂ if the recycling efficiency is shut off; similar effects may occur in presence of organics.

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In the section 3.5.4 the MS discussed the possible sources of uncertainties of the novel equation including the approximate calculation of HO₂ concentration gradients and the influence of organics. We added the words: “or high copper equivalent concentration.” in the first paragraph in this section.

About the influence of Fe ions is answered above.

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

215

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

Hu, J., Shi, Q., Davidovits, P., Worsnop, D., Zahniser, M., and Kolb, C.: Reactive uptake of Cl_{2(g)} and Br_{2(g)} by aqueous surfaces as a function of Br and I ion concentration: The effect of chemical reaction at the interface, *The Journal of Physical Chemistry*, 99, 8768-8776, 1995.

220

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

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

225

Macintyre, H., and Evans, M.: Parameterisation and impact of aerosol uptake of HO₂ on a global tropospheric model, *Atmos. Chem. Phys.*, 11, 10965-10974, 2011.

Magi, L., Schweitzer, F., Pallares, C., Cherif, S., Mirabel, P., and George, C.: Investigation of the uptake rate of ozone and methyl hydroperoxide by water surfaces, *The Journal of Physical Chemistry A*, 101, 4943-4949, 1997.

230

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

Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G.: Mass accommodation coefficient for HO₂ radicals on aqueous particles, *J. Geophys. Res.-Atmos.*, 92, 4163-4170, 10.1029/JD092iD04p04163, 1987.

Müller, B., and Heal, M. R.: The mass accommodation coefficient of ozone on an aqueous surface, *Physical Chemistry Chemical Physics*, 4, 3365-3369, 2002.

235

Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous loss of HO₂ by KCl, synthetic sea salt, and natural seawater aerosol particles, *Atmos. Environ.*, 43, 1660-1665, 2009.

Thornton, J., and Abbatt, J. P. D.: Measurements of HO₂ uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, *Journal of Geophysical Research: Atmospheres*, 110, 10.1029/2004JD005402, 2005.

240

Thornton, J. A., Jaegle, L., and McNeill, V. F.: Assessing known pathways for HO₂ loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, *Journal of Geophysical Research: Atmospheres*, 113, 2008.

Utter, R. G., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of the mass accommodation coefficient of ozone on aqueous surfaces, *J Phys Chem-Us*, 96, 4973-4979, 10.1021/j100191a045, 1992.

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

Huan Song^{1,2}, Xiaorui Chen^{1,2}, Keding Lu^{1,2*}, Qi Zou^{1,2}, Zhaofeng Tan^{2,3}, Hendrik Fuchs^{2,3}, Alfred Wiedensohler⁴, Daniel R. Moon^{5,6}, Dwayne E. Heard⁵, María-Teresa Baeza-Romero⁷, Mei Zheng¹, Andreas Wahner^{2,3}, Astrid Kiendler-Scharr^{2,3}, Yuanhang Zhang^{1,2}

1. State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China

2. International Joint Laboratory for Regional Pollution Control, Jülich, Germany, and Beijing, China

3. Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

4. Leibniz Institute for Tropospheric Research, 04318 Leipzig, Germany

5. School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

6. LISA, Université Paris-Est Créteil, Université de Paris, Faculté des Sciences et Technologie, 61 avenue du Général de Gaulle, 94010 Créteil Cedex, France

7. Universidad de Castilla-La Mancha, Escuela de Ingenieros de Industrial y Aeroespacial de Toledo, 45071, Toledo, Spain

Correspondence to: Keding Lu (k.lu@pku.edu.cn)

Abstract. Heterogeneous uptake of hydroperoxyl radicals (HO₂) onto aerosols has been proposed to be a significant sink of HO_x hence impacting the atmospheric oxidation capacity. Accurate calculation of the HO₂ uptake coefficient γ_{HO_2} is key to quantifying the potential impact of this atmospheric process. Laboratory studies show that γ_{HO_2} can vary by orders of magnitude due to changes in aerosol properties, especially aerosol soluble copper (Cu) concentration and aerosol liquid water content (ALWC). In this study we present a state-of-the-art model called MARK to simulate both gas and aerosol phase chemistry for the uptake of HO₂ onto Cu-doped aerosols. Moreover, a novel parameterization of HO₂ uptake was developed that considers changes in relative humidity (RH) and condensed phase Cu ion concentrations and which is based on a model optimization using previously published laboratory and new laboratory data included in this work. This new parameterization would be applicable to wet aerosols and it would complement current IUPAC recommendation ~~for cloud droplets~~. The new parameterization is as follows [\(the explanations for symbols- are in the Appendix\)](#):

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

All parameters used in the paper are summarized in Table A1. Using this new equation, field data from [Wangdu-a field campaign](#) were used to evaluate the impact of the HO₂ uptake onto aerosols on the RO_x (=OH + HO₂+RO₂) budget. Highly variable values for HO₂ uptake were obtained for North China Plain (median value <0.1).

1 Introduction

The atmospheric cleaning capacity of the troposphere is largely determined by the concentrations of the hydroxyl radical, which are closely linked with the concentrations of the 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/ $\text{CH}_4/\text{H}_2/\text{SO}_2$ and $\text{HO}_2 + \text{NO}$ (Seinfeld, 1986). The reactivity from aerosol uptake cannot compete with the known gas phase reactivity of OH, whereas it may compete with the reactivity of NO toward HO_2 under some conditions such as low NO (Tang et al., 2017). For high aerosol mass load, the reaction rate of HO_2 with aerosol particles could be fast enough to influence the concentration of HOx radicals, and consequently, reduce ozone production from $\text{HO}_2 + \text{NO}$ (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) and often the value of γ_{HO_2} (the heterogeneous uptake coefficient (Schwartz, 1984; Schwartz, 1986)) is assumed to be a single value, 0.2 (Tie et al., 2001; Martin et al., 2003). The ~~model results of: impact of~~ HO_2 uptake ~~influence~~ is lowered when a parameterized equation of γ_{HO_2} is used without considering the influence of transition metal ions (TMIs) (Thornton et al., 2008). ~~The reasons for the lower reactivity in absence of TMI including the lower reaction rate of aqueous HO_2/O_2^- reactions~~ (Thornton et al., 2008). ~~However, in spite of the lower HO_2 uptake coefficient used however, still,~~ a significant impact on the calculated [OH] and O_3 production rate are suggested for air masses over Chinese megacity areas (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 proposed that in the North China Plain (Li et al., 2019a; Li et al., 2019b), the reduced HO_2 uptake owing to reduction of aerosol surface area is considered to be the key reason for the increased surface ozone concentration over the last few years when a value of 0.2 was used for γ_{HO_2} .

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 liquid deliquesced aerosols. 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., 2016b; George et al., 2013). For fine particles, the reactions of HO_2 with soluble Cu ions may be fast enough, 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 pressing atmospheric issues such as ozone formation.

In this study, we reanalyzed several datasets of the aerosol uptake of HO_2 from laboratory studies reported in the literature, a new dataset for HO_2 uptake coefficient onto Cu-doped 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 laboratory

results. Furthermore, for Wangdu field campaign, we also calculated γ_{HO_2} according to the *NEq.* and the impact of HO_2 uptake on HO_x ($=OH + HO_2$) budget was evaluated.

2 Materials and Methods

2.1 The Model

310 A Multiphase Reaction Kinetic Model (MARK) is developed in this study for the simulation of γ_{HO_2} for the 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 averaged quasi-first order gas phase HO_2 uptake loss rate at steady state, k_{het} (s^{-1}), in Eq. (1). γ_{HO_2} is retrieved by Eq.(2) considering the influence of ~~in this model,~~ aerosol liquid water content (ALWC) [$g\ cm^{-3}$] is more pertinent rather than surface density because of the influence of the *RH* on the uptake process (Kuang et al., 2018; Bian et al., 2014).

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

$$k_{het} = \left(\frac{R_d}{D_g} + \frac{4}{\gamma v_{HO_2}} \right)^{-1} \times \frac{3ALWC}{\rho R_d} \quad (2)$$

320 The meanings of the symbols are summarized in the Appendix. The units of aqueous reagents are converted to [$molecule\ cm^{-3}$] in the model by k_{mt} . To combine both gas phase molecular diffusion and liquid phase interface mass transport processes the approach adopted is using 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 given by equation (3):

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

325 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 $>1\ \mu m$), k_{mt} is mainly determined by gas phase diffusion of HO_2 . For smaller particles (radius $<1\ \mu m$) k_{mt} is
330 mainly determined by the accommodation process. 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, an effective Henry's law constant H^{cc} should be applied in the model calculation, that takes into account the effects of solution pH and "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
335 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 to γ_{HO_2} in the MARK model

340 2.2.1 Henry's law of gas phase reactants

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_0 is estimated to be about 3900 M atm^{-1} at 298K for HO_2 (Thornton et al., 2008; Golden et al., 1990; Hanson et al., 1992) and its temperature dependence is given accordingly to the IUPAC recommendation (Ammann et al., 2013; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>). H_0 should be corrected by the solution pH and the “salting out” effect. In the MARK model, these two corrections are incorporated as H^{cc} :

$$H^{cc} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right) \times A_{\text{HO}_2} = 9.5 \times 10^{-6} \exp\left(\frac{5910}{T}\right) \times \left(1 + \frac{K_{eq}}{[H^+]}\right) \times A_{\text{HO}_2} \quad (4)$$

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):

$$A = 10^{-0.1 \times I} \quad (5)$$

According to this correction, H^{cc} of HO_2 increases with RH . The ratio of $-H^{cc}$ to H_0 ranges from 0.03 (40% RH , $I=16.7$) to 0.34 (80% RH , $I=5.5$). Although the salting effect and the ionic strength are mainly driven by $[\text{NH}_4^+]$ and $[\text{SO}_4^{2-}]$, ionic strength increases quickly from 5.9 to 9.5 with $[\text{Cu}^{2+}]$ from 0.1 M to 1 M and limits the solubility of HO_2 gas molecules.
and decreases quickly after $[\text{Cu}^{2+}]$ reaches 0.1M in aerosol liquid phase, which limits γ_{HO_2} at high Cu^{2+} concentration.

2.2.2 Aerosol 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 ALWC and aerosol particle condensed phase component concentrations. In this work ISORROPIA II (Fountoukis and Nenes, 2007; Capps et al., 2012) thermodynamic equilibrium model for inorganic aerosol systems is used to take into account this.

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

Since there is no direct evidence of the existence of Cu/Fe redox reactions of HO₂ which produce H₂O rather than H₂O₂ as proposed by (Mao et al., 2013), in the scope of this paper, HO₂ uptake produce H₂O separately by Cu and Fe free ions as proposed by many researches (Mozurkewich et al., 1987; Hanson et al., 1992; Thornton and Abbatt, 2005a; Thornton et al., 2008; Taketani et al., 2009; Macintyre and Evans, 2011). Fe free ions can be seen as the equivalent Cu free ions in the application of the MARK model or the parameterized equation mentioned below.

Based on Ross and Noone (Ross and Noone, 1991), for an ion (x_i) of charge z_i ($i=x,y,z,\dots$), the activity coefficient (φ_x) is

$$\log \varphi_x = -z_x^2 D - \sum_y \varepsilon(x, y, I) m_y \quad (6)$$

where D is given by equation (7):

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

I is the ionic strength of a solution [M], which can be calculated as following equation:

$$I = \frac{1}{2} \cdot \sum m_i \cdot z_i^2 \quad (8)$$

$\varepsilon(x, y, I)$ 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, $\varepsilon(x, y, I)$ 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):

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

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

$$[x_i]_{\text{effective}} = [x_i] \times \varphi_{x_i} \quad (10)$$

In the aerosol particle condensed phase, an effective concentration rather than the total concentration of Cu ion should be calculated in catalytic aqueous reactions with HO₂. The effective concentration of ~~Cu ion TMI~~ can be calculated as:

$$[Cu^{2+}]_{\text{effective}} = ([Cu^{2+}] + [Cu^{2+}]_{\text{equ}}) \times \varphi_{Cu} \quad (11)$$

$[Cu^{2+}]_{\text{eff}}$ is the effective aerosol condensed phase soluble copper concentration. In this paper, $[Cu]_{\text{equ}}$ represents the equivalent copper concentrations from other TMI such as Fe and Mn.

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

Gas phase HO₂ molecules dissolve in the particle condensed phase and diffuse from the surface of a particle toward the center in parallel with aqueous phase reactions. We need to evaluate $[\overline{HO_2}]$, the assumed averaged steady-state HO₂ concentration over the volume of the particle. $[HO_{2(r)}]$ is HO₂ concentration at the surface of particles. The ratio of these two concentrations can be calculated as (Schwartz, 1986; Schwartz, 1984):

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

where q is given by equation (13):

$$q = R_d \times \left(\frac{k_{eff}}{D_{aq}}\right)^{0.5} \quad (13)$$

and D_{aq} is the aqueous phase diffusion coefficient [cm^2s^{-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. k_{eff} is calculated by Eq.19 and includes the influence of the salting out effect of HO_2 and the ionic strength effects on TMI. k_{eff} will change dramatically according to the concentration of equivalent copper ions and the diameter of particles. Higher Cu concentration will make the ratio smaller and cause larger uncertainties, however, in the copper-doped aerosol particle, because of the high value of k_{eff} (typical value is $2.9 \times 10^6 \text{ M s}^{-1}$ with 1 M Cu^{2+} and $3.25 \times 10^4 \text{ M s}^{-1}$ with 0.001 M Cu^{2+}) and small Count Median Diameter (R_d) (usually smaller than $1 \mu\text{m}$), the ratio $\frac{[\text{HO}_2]}{[\text{HO}_2(r)]}$ is close to 1. At a diameter of ~~1 μm~~ 100nm, and a relative humidity between 40% and 90%, the condensed phase copper ion concentration varies from 10^{-5} to 1 M , the average ratio of the surface HO_2 concentration and the condensed phase HO_2 concentration is beyond 0.87 at every Cu concentration.0.89. ~~At 400 nm diameter particles for RH = 40% to 90%, the ratio is larger than 0.95.~~ The ratios are calculated by simulation of k_{eff} and the accordingly calculations by Equation (12) and (13). Thus, in this model, we assume the surface concentration of HO_2 equals to the condensed phase average HO_2 concentration.

410 2.3 Laboratory results for the HO_2 accommodation coefficient

The accommodation coefficient of HO_2 (α_{HO_2}) ~~used in the model is independent of the concentrations of free Cu ions if the viscosity of particles maintains. While the more accurate accommodation coefficient can be only measured with no limitation of aqueous mass transfer flux, in which situation, α_{HO_2} equals to γ_{HO_2} .~~ HO_2 uptake coefficients are summarized ~~was determined~~ for copper-doped inorganic aerosol particles ~~using values taken~~ from various previous laboratory studies. The uptake coefficient of HO_2 is accommodation coefficient of HO_2 (α_{HO_2}) is approximately 0.5 in sulfate aerosol and even higher for chlorine or nitrate aerosol because of the catalytic effect of Cu^{2+} on aqueous HO_2/O_2^- (Table 1). In this situation, the aqueous reactions are fast enough for the uptake process be limited primarily by the mass transport process (accommodation) and the uptake coefficient equals to the accommodation coefficient. ~~With the wide distribution of Cu^{2+} in aerosol particles, a high accommodation coefficient of HO_2 presents the possibility of HO_2 uptake as an important sink of 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 uses~~ uses the accommodation coefficient 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.

425 Table 1: γ_{HO_2} determined under laboratory conditions for copper-doped inorganic aerosols.

Aerosol type	RH/%	Estimation of [Cu] in aerosol (mol L ⁻¹)	$\gamma_{HO_2} \propto \frac{[Cu]}{[HO_2]}$	Ref.
NH ₄ HSO ₄	75%	0.0059–0.067*	0.40 ± 0.21	(Mozurkewich et al., 1987)
(NH ₄) ₂ SO ₄	45%	0.5	0.53 ± 0.13	(Taketani et al., 2008)
(NH ₄) ₂ SO ₄	42%	0.16	0.5 ± 0.1	(Thornton and Abbatt, 2005b)
(NH ₄) ₂ SO ₄	53–65%	0.5–0.7*	0.4 ± 0.3	(George et al., 2013)
(NH ₄) ₂ SO ₄	65%	0.57	0.26 ± 0.02	(Lakey et al., 2016b)
(NH ₄) ₂ SO ₄	51%	0.0027	0.096 ± 0.024	(Zou et al., 2019)
(NH ₄) ₂ SO ₄	43%	0.38	0.355 ± 0.023	This work
NaCl	53%	~0.5	0.65 ± 0.17	(Taketani et al., 2008)
KCl	75%	5% of KCl solution	0.55 ± 0.19	(Taketani et al., 2009)
LiNO ₃	75%	0.03–0.0063*	0.94 ± 0.5	(Mozurkewich et al., 1987)

*Cu concentration is in molality (M).

2.4 The experimental setup and methodology of the latest results of γ_{HO_2}

In this study, we also ~~conclude~~ included 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., 2018; Lakey et al., 2016b; George et al., 2013) and so only brief details are given here. In summary, the experiments were performed by moving an HO₂ injector backwards and forwards along the concentric axis of a laminar aerosol flow tube hence changing the contact time between HO₂ and the aerosols. Measurements of [HO₂] 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-Scanning Mobility Particle Sizer (SMPS) at the end of the flow tube. Aerosol particleless were ~~formed~~ produced 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(HO₂ signal) against the interaction time between HO₂ 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.

3 Results and Discussion

3.1 Parameter sensitivity analysis of the MARK model

Hygroscopic inorganic particles are one of the most important components of $PM_{2.5}$ in ambient air. The annual average contribution of inorganic aerosol to $PM_{2.5}$ is between 25% and 48% across China (Tao et al., 2017), especially NH_4^+ , SO_4^{2-} , NO_3^- and other inorganic ions. In laboratory studies of radical heterogeneous reactions, $(NH_4)_2SO_4$ aerosol is most widely studied because of its simple components, easy way to generate 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 to derive a parameterized equation for the uptake coefficient, γ_{HO_2} .

In this study, $(NH_4)_2SO_4$ aerosol uptake reactions of HO_2 are 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 (for the lack of measured data the parameterized equation is only valid in the range of 40% to 90% RH).

Figure 1 shows the influences of both factors, RH and condensed phase pH together with Cu^{+2} concentration on the heterogeneous process of HO_2 . As the RH rises, the γ_{HO_2} exhibits a logarithmic growth. Higher RH means a higher water content which dilutes the bulk phase ions thus promotes the activity coefficients of reactant ions in the aerosol particle condensed phase and the solubility of the gas phase reactant such as OH , HO_2 and H_2O_2 .

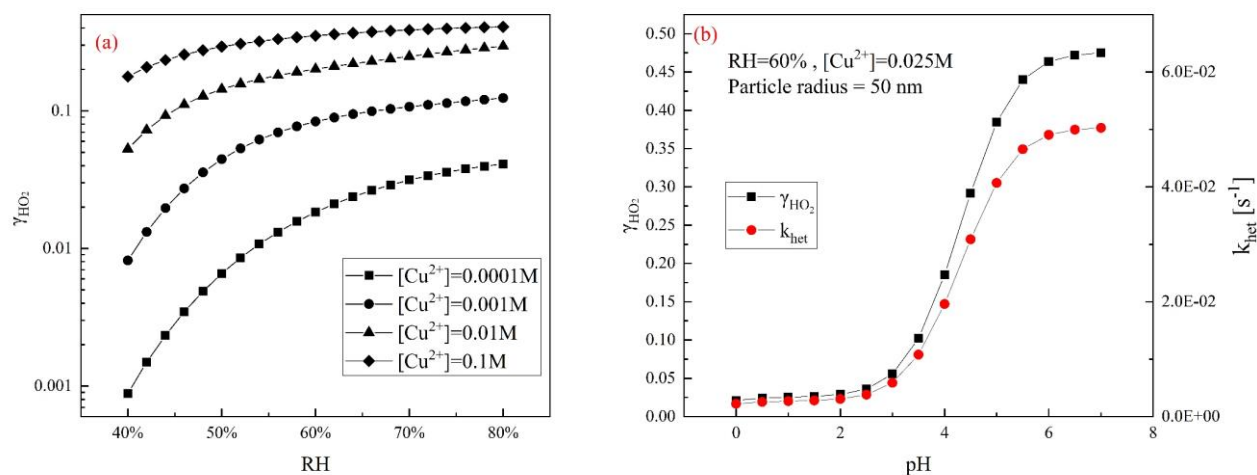


Figure 1: Influence of various parameters upon γ_{HO_2} predicted by the MARK model. (a) γ_{HO_2} increases with the RH at different $[Cu^{2+}]$; (b) γ_{HO_2} denoted by black squares and black line and k_{het} in red circles and red line increase with aerosol particle condensed phase pH.

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

3.2 Model Validation

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, 2005b) 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 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 (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 $1-2 \times 10^{-4}$ M, the heterogeneous uptake of HO_2 is not significant and may mainly be driven by the self-reaction of HO_2 . This threshold is consistent with the results of previous researches (Mozurkewich et al., 1987; Lakey et al., 2016b). The threshold is also consistent in different heterogeneous media of aerosol and cloud or rain droplets. As the copper concentration increases, the solution ionic strength increases and, γ_{HO_2} rapidly rises to the limit of the accommodation coefficient and determined by the limitation of 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 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:

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

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

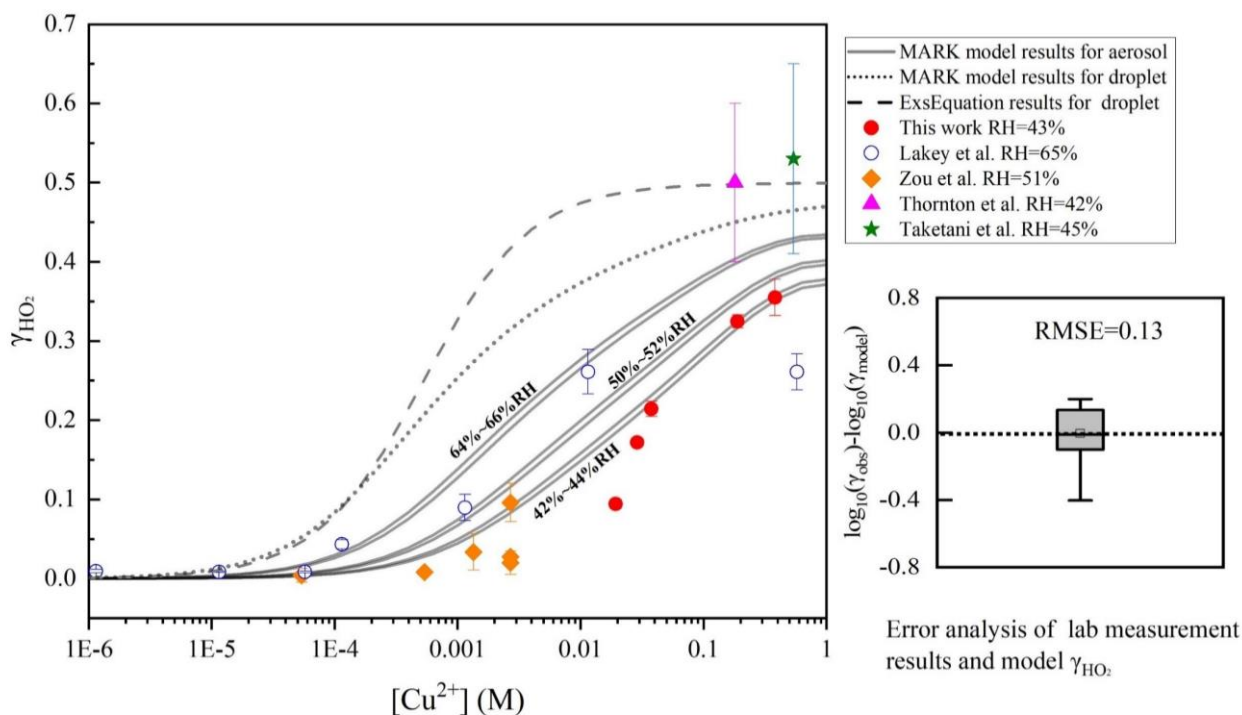


Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red filled circles denote the results at 43% RH measured at Leeds included in this paper. Blue hollow circles at 65% RH (Lakey et al., 2016b). Yellow filled diamonds denote results at 51% RH (Zou et al., 2019), filled purple triangle at 42% RH (Thornton and Abbatt, 2005b) and filled green star at 45% RH (Taketani et al., 2008). The grey dashed line denotes the results of the classical parameterized equation- (named as *CEq.* in this paper) γ_{HO_2} with [deliquesced aerosol particles/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 (Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002; Hu et al., 1995). The

515 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/>).

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3.3 Comparison of the classical parameterized equation and the MARK model

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.>) [proposed for \$HO_2\$ uptake for deliquesced aerosol particles](#)—has been proved to provide good
 525 estimation of reactive gas molecular uptake coefficient on dilute solution droplets (Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002; Hu et al., 1995).

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

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

530 When the classical parameterized equation ($CEq.$) is applied to the calculate HO_2 uptake coefficient with [copper-doped](#) 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
 535 constant of HO_{2_total} ($=HO_{2(aq)} + O_{2^-(aq)}$) with Cu ions as $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ rather than the more commonly used value of $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ considering the pH limitation (pH is about 3-5 in ambient aerosol particle condensed phase as discussed above). The prior value ($1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) reflects the rate of reaction between HO_2 and Cu^{2+} , more prevalent in acidic aerosol such as ammonium sulfate, and the latter ($1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) 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
 540 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 $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ to achieve the best fit based on the calculation results from Lakey et al. (2016b). ~~This assumption is not in accordance with the aqueous reaction rate coefficient from other databases mentioned below and needs further laboratory measurements to confirm it. According to the aqueous reaction rate coefficient from NIST and the latest measurement result (Lundström et al., 2004;~~
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Huie, 2003), the rate coefficient of HO₂ with Cu²⁺ is 1×10⁸ or 1.2×10⁹ M⁻¹s⁻¹ at pH=2 and pH=1, respectively. These two rate coefficients were quantified in a low pH environment (pH=2 for 1.2×10⁹ M⁻¹s⁻¹ and pH=1 for 1×10⁸ M⁻¹s⁻¹). At the same time, the reaction rate of O₂⁻ with Cu²⁺ is 8×10⁹ M⁻¹s⁻¹ for pH in the range 3-6.5 (Huie, 2003). At higher pH, the reaction rate of HO₂ with Cu²⁺ 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 Cu²⁺ ions with HO₂ and O₂⁻ in aqueous solution. The low reaction rates used here in the CEq. are assumed to likely result from the combined effects of solute strength effects as discussed by Lakey et al. (2016b). The MARK model uses the same framework with the CEq. and considers the Setchenov salting out and ionic strength effects on HO₂ uptake more comprehensively and detailly and proposes k_{eff} as the effective reaction coefficient (Eq.19).

The rate constants used in the MARK model are shown in the Table S. 1 in the SI. The reaction rate of Cu²⁺ with HO₂/O₂⁻ is 1×10⁸ and 8×10⁹ M⁻¹s⁻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 [Cu²⁺] and RH on γ_{HO_2} .

3.4 A novel parameterized equation of γ_{HO_2}

When the full reaction system reaches steady-state, the reaction of HO₂ in the aqueous particle phase can be expressed as the following reaction scheme (Schwartz, 1984; Schwartz and Freiberg, 1981; Schwartz, 1987):



Gas phase HO_{2(g)} molecule transports onto the surface of the aerosol particles, HO_{2(r)} then dissolves at the condensed phase to give HO_{2(a)}. The reactions between Cu²⁺/Cu⁺ and HO₂ can be seen as catalytic reactions, because in the model simulations, the total amount of [Cu²⁺]+[Cu⁺] does not change with reaction time. The rate of HO₂ aqueous reaction with copper ions is noted as k_{eff} . For fine particles, we can safely assume that the interface concentration [HO_{2(r)}] is equal to the condensed phase average $\overline{[HO_2]}$ concentration due to rapid diffusion in the liquid phase (details have been 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 surface concentration of the reactant, $c_{g,surf}$ is the gas phase concentration. In the process of HO₂ uptake, we deduce the parameterized equation (NEq.) of γ_{HO_2} in the framework of the resistance model:

$$\frac{1}{\gamma} = \frac{1}{\alpha_{HO_2}} + \frac{3 \times v_{HO_2}}{4 \times R_d \times H_{corr} \times RT k_{eff}} \quad (18)$$

$$k_{eff} = f(ALWC, PM) \times [Cu^{2+}]_{eff}^{0.65} \quad (19)$$

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

$$580 \quad \cancel{[Cu^{2+}]_{equ} = [Cu^{2+}]^\phi = [Cu^{2+}]^{0.65}} \quad (21)$$

From Eq.-(18), 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) 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. k_{eff} is related to ~~the~~ $[Cu^{2+}]_{eff}$, which is the sum of condensed phase soluble copper concentration $[Cu^{2+}]$ and other equivalent copper – concentrations mentioned Eq.11, with an exponential relationship to the parameterization ~~of the catalytic reactions, which is denoted in Eq. (19).~~ The exponent of $[Cu^{2+}]_{eff}$ is globally fitted using the MIPFIT method. It is found that the overall R^2 is higher than 0.97 and the residual is minimized when the exponent is 0.65. $f(ALWC, [PM])$ has a negative exponential relationship to $[PM]$, and has a positive linear relationship to RH .

590 We further calculated the RMSE of the modeled data and $NEq.$ (Eq.15) data under different RH conditions. The range of values shows the difference between the modeled data and $NEq.$ data at different Cu^{2+} concentration. At low RH and consequently relatively low ALWC, γ_{HO_2} is more sensitive to $[Cu^{2+}]$ especially at low $[Cu^{2+}]$. This sensitivity 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.

595 All the RMSE values are smaller than 0.2, which indicates a minor deviation from the laboratory results in our γ_{HO_2} equation. In the typical ambient urban atmospheric environment, with an aerosol mass concentration of 10-300 $\mu g m^{-3}$, aqueous Cu^{2+} concentration of 10^{-5} -1 molar concentration, and a relative humidity between 40%-90%, the $NEq.$ can be used. Beyond the range, the application of the $NEq.$ 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; 600 Kanaya et al., 2009; Taketani and Kanaya, 2010; Thornton et al., 2008; George et al., 2013).

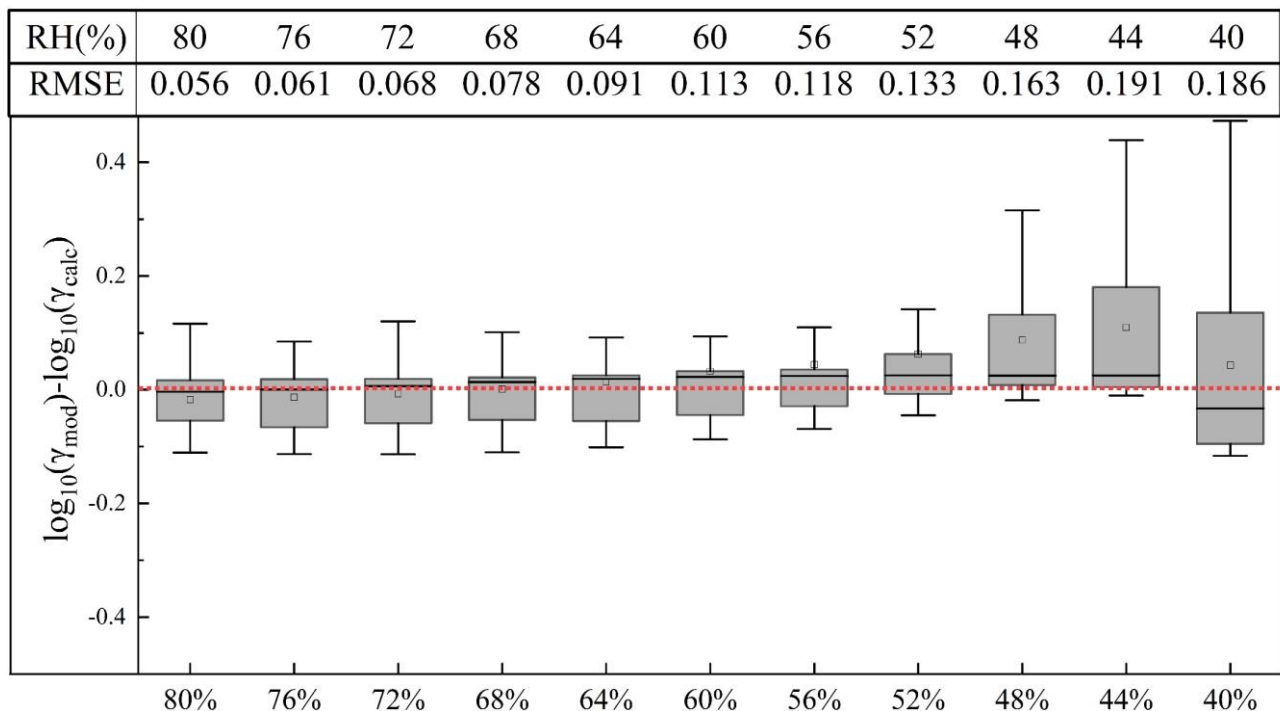


Figure 3: Comparison of the MARK modeled γ_{HO_2} to the corresponding calculated values from the *NEq*. $\log_{10}(\gamma_{mod})$ is the logarithmic value of modeled γ_{HO_2} and $\log_{10}(\gamma_{calc})$ is the calculated value from the *NEq*.

3.5 Evaluation of the impact of the new HO₂ uptake parametrization in the Wangdu campaign

605 Many model studies (Lakey et al., 2015; Martinez et al., 2003; Tie et al., 2001; Whalley et al., 2015) suggest that heterogeneous uptake of HO₂ radical affects the global distribution of trace gases and the atmospheric oxidant capacity especially in regions with high aerosol loading or low NO_x 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 HO₂ with aerosol and gas phase reactants is crucial when evaluating the influence of heterogeneous reactions
610 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 (Tan et al., 2020), the HO₂ uptake coefficient and the ratios of the HO₂ uptake loss rates ($TR_{HO_2\text{uptake}}$) to the sum of the RO_x termination rates ($TR_{RO_x\text{sinks}}$) are calculated with direct measurements of the RO_x radicals, trace gas species, ALWC and the aerosol condensed phase component concentrations (please see the SI for details). The experimental determined RO_x
615 termination rates include reaction channels from OH + NO₂, OH + NO, HO₂ + HO₂, HO₂ + RO₂ and RO₂ + NO. Considering

the solubility and size distribution of particle metal copper (Fang et al., 2017; Hsu et al., 2010a; Mao et al., 2013) we can estimate γ_{HO_2} in daytime and night.

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

620 Wangdu is located in the center of the Beijing-Tianjin-Hebei area and it is a regional site. The observations were carried out in the summer with serious photochemical smog 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 environment with a monsoon climate.

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

Parameters	Average values	1 σ Accuracy
Temperature / $^{\circ}$ C	27 \pm 4	\pm 0.05%
Pressure /hPa	1000 \pm 5	\pm 0.05%
RH/%	61 \pm 18	\pm 0.05%
O ₃ /ppb	55.6 \pm 9.0	\pm 5%
NO _x /ppb	10 \pm 13.6	\pm 20%
HONO/ppb	0.8 \pm 0.24	\pm 20%
CO/ppm	0.6 \pm 0.19	<5%
Isoprene/ppb	0.5 \pm 0.11	\pm 15%-20%
HCHO/ppb	7 \pm 0.69	\pm 5%

3.5.2 Calculation of soluble copper ion concentration

630 During this campaign, the total concentration of heavy metal ions in fine particles (smaller than 2.5 μ m) was measured using a commercial instrument based on non-destructive X-ray fluorescence technique (Xact 625, Cooper Environmental). Since the concentration of soluble copper concentration rather than total copper concentration is used in the model, it is necessary to analyze the ratio of soluble copper to total copper in the aerosol particles. For particle radius smaller than 2.5 μ m, which are the most contributing bins of aerosols in HO₂ uptake, the mass fraction of Cu is about 33%–100% compared with other two size bins in ambient aerosols (2.5-10 μ m, >10 μ m) (Mao et al., 2013). 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 635 (Fang et al., 2017; Hsu et al., 2004; Hsu et al., 2010b). Therefore, when using the *NEq.* to calculate the HO₂ 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 hourly resolution total copper concentration (ng m^{-3}) is divided by the aerosol volume concentration and the atomic mass of copper (64) to obtain the total copper molar concentration in the aerosol (mol L^{-1}). γ_{HO_2} rather depends on copper concentration so we also evaluate the influence of copper solubility on the uptake coefficient. What is more, the unequally distribution of copper ions will also influence the HO_2 uptake coefficient (details in the SI).

3.5.3 γ_{HO_2} estimated at Wangdu field campaign

By inputting the soluble copper concentration, aerosol mass concentration, aerosol particle geometric mean diameter and the corresponding relative humidity and temperature into the *NEq*, we can obtain an estimation of γ_{HO_2} in suburban Wangdu, which is shown in Fig. 4 (a) and (b). The time resolution 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 $67.2 \pm 39.7 \mu\text{g m}^{-3}$, the average Cu concentration is $35.8 \pm 57.7 \text{ng m}^{-3}$. The results of a fit to a Gaussian function results in a γ_{HO_2} value of 0.116 ± 0.086 (1σ) the Wangdu campaign (γ_{HO_2} will increase from 0.065 ± 0.051 (1σ) at 10% solubility to 0.196 ± 0.142 (1σ) at 70% solubility for the summary of day and night data).

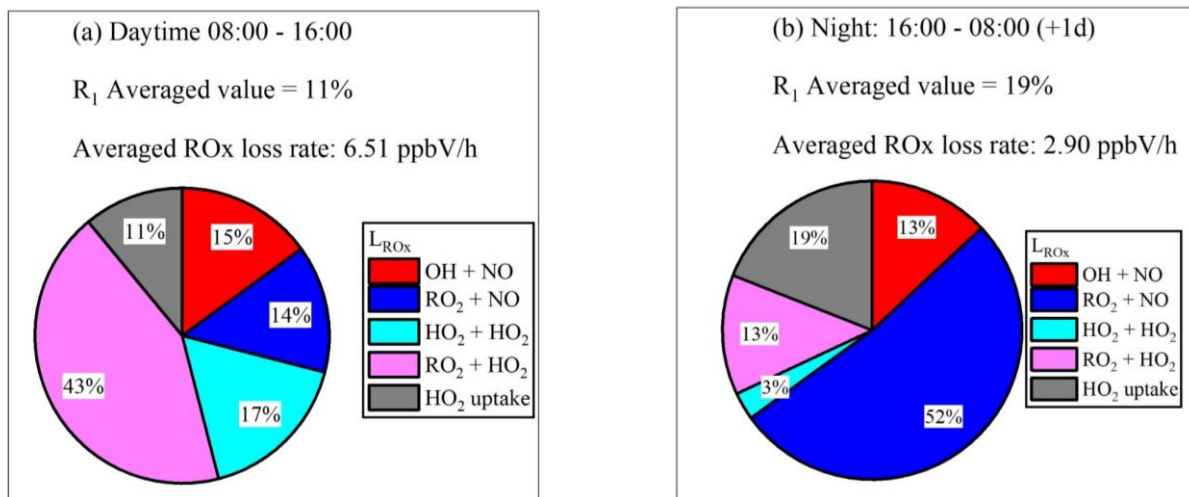
Tan et al. (2017) had compared the measured and modelled OH, HO_2 and RO_2 radicals in the Wangdu campaign. However, in this paper, they did not discuss the influence of HO_2 uptake. A very recent publication (Tan et al., 2020) calculated γ_{HO_2} in the Wangdu campaign based on the comparison of field measurement data for HO_2 and concentrations calculated by the box model. The paper proposes that all γ_{HO_2} calculated in this way from the Wangdu campaign can be fitted to a Gaussian distribution around the value of 0.08 ± 0.13 (1σ). This value is in the range of our estimation in this paper considering the influence of aerosol morphology and the indirect measurement uncertainty (please see the SI).

The experimentally determined RO_x 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 ($L_{HO_2\text{uptake}}$) to the whole RO_x loss rate (L_{RO_x}) is calculated by ~~Equation Eq. (212)~~ and ~~Eq.(223)~~.

$$L_{HO_2\text{uptake}} = 0.25 \cdot v_{HO_2} \cdot [ASA] \cdot [HO_2] \quad (212)$$

$$R_1 = \frac{L_{HO_2\text{uptake}}}{L_{RO_x}} \quad (223)$$

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



665

Figure 4: R_1 calculated by the *NEq.*. Pie charts show the values of R_1 and the loss rates for ROx during daytime (a) and nighttime (b). The averaged daytime (08:00–16:00) ROx radical loss rate is 6.5 ppbV/h and that for nighttime (16:00–08:00 (+1d)) is 2.9 ppbV/h.

670 No significant difference of γ_{HO_2} is observed during daytime and night. 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 a). However, HO_2 uptake may be important in the termination of ROx radicals at night shown in Fig. (4 b). The daytime ratio R_1 is lower than it is at night because of the

675 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

680 budget of ROx as shown in Fig (4 a), 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

685 may not crystallize immediately but may constitute a supersaturated aqueous solution (i.e., in the metastable state) (Song et al.,

2018)). The approximate calculation of HO₂ concentration gradients within the aerosol particle condensed phase also cause deviations for larger particles or high copper equivalent concentration. -

690 Organic content of an aerosol particle may affect several important parameters in the uptake model (Lakey et al., 2016b; Lakey et al., 2015). For example, the aerosol pH, hygroscopic properties of the aerosol, the rate of diffusion of HO₂ within the aerosol and a reduction in the concentration of Cu²⁺ via the formation of complexes that could affect the ability of Cu to undergo redox reactions with HO₂ and O₂⁻. 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 HO₂ 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.

695 Another uncertainty comes from aerosol particles morphology. The bulk diffusion coefficient of HO₂ and other reactive molecules should be lower in the situation of semi-solid particles (Berkemeier et al., 2016; Shiraiwa et al., 2010; Mikhailov et al., 2009) and would change with the water activity and the organic components (Price et al., 2015). For crystalline or amorphous solid aerosol particles, HO₂ will undergo surface reactions and diffuse across the surface rather than be accommodated within the aerosol bulk. The MARK model has limitations in the calculation of γ_{HO_2} with semi-solid aerosol
700 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 HO₂. The uptake process would vary with mixing state of the particles, thus the predicted
705 γ_{HO_2} values here may be biased as a 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., 2016a; Lakey et al., 2015; Lakey et al., 2016b) have also shown that the addition of an organic compound to Cu²⁺ doped aerosols such as oxalic acid, which forms oxalate ions (C₂O₄)²⁻ in the aerosol, results in a lower value of γ_{HO_2} as such ions forms a complex with the TMI.

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

4 Summary and conclusions

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
715 between 0.09 and 0.40, while those at Mt. Mang were between 0.13 and 0.34. 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 HO₂ 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 coefficient of 0.2 in their model calculations. However, the results of the MARK model and of the *NEq.* in this paper suggest that the HO₂ 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 HO₂ on gas phase and heterogeneous physicochemical reactions under different environmental conditions in different regions. The novel parameterized equation proposed in this paper provides an effective way for more detailed calculation of the effects of HO₂ 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 HO₂ 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 HO₂ uptake process needs to be considered in photochemical box models for the study of the HO_x 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 TMI, organic content, as well as the aerosol liquid water should be added for future field campaigns for the study of the HO_x radical budget.

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	-
v_{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	mol cm ⁻³ atm ⁻¹
	$H_{corr} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right)$	
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}	μg 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	-
$[x_i]_{eff}$	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

Author Contribution

735 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 Mar á-Teresa Baeza-Romero contributed the laboratory
740 studies of HO₂ uptake coefficients, and they have contributed to writing the manuscript. Huan Song performed the model
simulations and prepared the manuscript with Keding Lu and Zhaofeng Tan which was enhanced by contributions from all the
co-authors.

Competing Interest

The authors have no conflict of interests.

Data Availability

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

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References

- Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated
kinetic and photochemical data for atmospheric chemistry: Volume VI - heterogeneous reactions with liquid substrates, *Atmos.*
Chem. Phys., 13, 8045-8228, 10.5194/acp-13-8045-2013, 2013; IUPAC Task Group on Atmospheric Chemical Kinetic Data
755 Evaluation, <http://iupac.pole-ether.fr>.
Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Pöschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy,
semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, *Physical*
Chemistry Chemical Physics, 18, 12662-12674, 2016.
Bian, Y. X., Zhao, C. S., Ma, N., Chen, J., and Xu, W. Y.: A study of aerosol liquid water content based on hygroscopicity
760 measurements at high relative humidity in the North China Plain, *Atmos. Chem. Phys.*, 14, 6417-6426, 10.5194/acp-14-6417-
2014, 2014.
Bielski, B. H., Cabelli, D. E., Arudi, R. L., and Ross, A. B.: Reactivity of HO₂/O₂⁻ radicals in aqueous solution., *Journal of*
physical and chemical reference data, 14, 1041-1100, 1985.

- 765 Capps, S., Henze, D., Hakami, A., Russell, A., and Nenes, A.: ANISORROPIA: the adjoint of the aerosol thermodynamic model ISORROPIA, *Atmospheric Chemistry & Physics*, 12, 2012.
- Chameides, W. L., and Stelson, A. W.: Aqueous-phase chemical processes in deliquescent seasalt aerosols, *Ber Bunsen Phys Chem*, 96, 461-470, 1992.
- Cheng, M. C., You, C. F., Cao, J. J., and Jin, Z. D.: Spatial and seasonal variability of water-soluble ions in PM_{2.5} aerosols in 14 major cities in China, *Atmos. Environ.*, 60, 182-192, 10.1016/j.atmosenv.2012.06.037, 2012.
- 770 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H⁺-NH₄⁺-SO₄²⁻-NO₃⁻-H₂O at tropospheric temperatures, *Journal of Physical Chemistry A*, 102, 2137-2154, 10.1021/jp973042r, 1998.
- Cooper, P. L., and Abbatt, J. P. D.: Heterogeneous interactions of OH and HO₂ radicals with surfaces characteristic of atmospheric particulate matter, *J Phys Chem-Us*, 100, 2249-2254, Doi 10.1021/Jp952142z, 1996.
- 775 Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, *Atmos. Chem. Phys.*, 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.
- Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, *Environ. Sci. Technol.*, 51, 2611-2620, 10.1021/acs.est.6b06151, 2017.
- Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K⁺-Ca²⁺-Mg²⁺-NH₄⁺-Na⁺-SO₄²⁻-NO₃⁻-Cl-H₂O aerosols, *Atmos. Chem. Phys.*, 7, 4639-4659, 2007.
- 780 George, I. J., Matthews, P. S. J., Whalley, L. K., Brooks, B., Goddard, A., Baeza-Romero, M. T., and Heard, D. E.: Measurements of uptake coefficients for heterogeneous loss of HO₂ onto submicron inorganic salt aerosols, *Physical Chemistry Chemical Physics*, 15, 12829-12845, 2013.
- Golden, D. M., Bierbaum, V. M., and Howard, C. J.: Re-evaluation of the bond-dissociation energies (Delta-Hd₀) for H-OH, H-OOH, H-OO-, H-O-, H-OO-, and H-OO, *J Phys Chem-Us*, 94, 5413-5415, 10.1021/j100376a046, 1990.
- 785 Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, *Sci Rep-Uk*, 7, 12109, 10.1038/s41598-017-11704-0, 2017.
- Hanson, D. R., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of OH and HO₂ radical uptake coefficients on water and sulfuric-acid surfaces, *J Phys Chem-Us*, 96, 4979-4985, Doi 10.1021/J100191a046, 1992.
- 790 Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric-acid aerosol: A framework for model calculations, *J. Geophys. Res.-Atmos.*, 99, 3615-3629, 10.1029/93jd02932, 1994.
- Heard, D. E., and Pilling, M. J.: Measurement of OH and HO₂ in the troposphere, *Chemical Reviews*, 103, 5163-5198, 10.1021/cr020522s, 2003.
- 795 Hsu, S.-C., Wong, G. T. F., Gong, G.-C., Shiah, F.-K., Huang, Y.-T., Kao, S.-J., Tsai, F., Candice Lung, S.-C., Lin, F.-J., Lin, I. I., Hung, C.-C., and Tseng, C.-M.: Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea, *Marine Chemistry*, 120, 116-127, <https://doi.org/10.1016/j.marchem.2008.10.003>, 2010a.
- Hsu, S. C., Liu, S. C., Lin, C. Y., Hsu, R. T., Huang, Y. T., and Chen, Y. W.: Metal compositions of PM₁₀ and PM_{2.5} aerosols in Taipei during spring, 2002, *Terrestrial Atmospheric and Oceanic Sciences*, 15, 925-948, 10.3319/tao.2004.15.5.925(adse), 2004.
- 800 Hsu, S. C., Liu, S. C., Tsai, F., Engling, G., Lin, H., Chou, C. K. C., Kao, S. J., Lung, S. C. C., Chan, C. Y., Lin, S. C., Huang, J. C., Chi, K. H., Chen, W. N., Lin, F. J., Huang, C. H., Kuo, C. L., Wu, T. C., and Huang, Y. T.: High wintertime particulate matter pollution over an offshore island (Kinmen) off southeastern China: An overview, *J. Geophys. Res.-Atmos.*, 115, 10.1029/2009jd013641, 2010b.
- 805 Hu, J., Shi, Q., Davidovits, P., Worsnop, D., Zahniser, M., and Kolb, C.: Reactive uptake of Cl_{2(g)} and Br_{2(g)} by aqueous surfaces as a function of Br⁻ and I⁻ ion concentration: The effect of chemical reaction at the interface, *The Journal of Physical Chemistry*, 99, 8768-8776, 1995.
- Huie, R. E.: NDRL/NIST Solution Kinetics Database on the WEB, *Journal of Research (NIST JRES)*-, 108, 2003.
- Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 34, 2131-2159, 10.1016/s1352-2310(99)00462-8, 2000.
- 810 Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Tanimoto, H., Kato, S., Suthawaree, J., Inomata, S., Taketani, F., Okuzawa, K., Kawamura, K., Akimoto, H., and Wang, Z. F.: Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors, *Atmos. Chem. Phys.*, 9, 7711-7723, 2009.

- 815 Kolb, C., Worsnop, D., Zahniser, M., Davidovits, P., Keyser, L., Leu, M.-T., Molina, M., Hanson, D., Ravishankara, A., and Williams, L.: Laboratory studies of atmospheric heterogeneous chemistry, in: Progress and problems in atmospheric chemistry, World Scientific, 771-875, 1995.
- Kuang, Y., Zhao, C. S., Zhao, G., Tao, J. C., Xu, W. Y., Ma, N., and Bian, Y. X.: A novel method for calculating ambient aerosol liquid water content based on measurements of a humidified nephelometer system, *Atmos Meas Tech*, 11, 2967-2982, 10.5194/amt-11-2967-2018, 2018.
- 820 Kuang, Y., Tao, J., Xu, W., Yu, Y., Zhao, G., Shen, C., Bian, Y., and Zhao, C.: Calculating ambient aerosol surface area concentrations using aerosol light scattering enhancement measurements, *Atmos. Environ.*, 216, 116919, <https://doi.org/10.1016/j.atmosenv.2019.116919>, 2019.
- Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO₂ Uptake Coefficients onto Single Component Organic Aerosols, *Environ. Sci. Technol.*, 49, 4878-4885, 10.1021/acs.est.5b00948, 2015.
- 825 Lakey, P. S. J., Berkemeier, T., Krapf, M., Dommen, J., Steimer, S. S., Whalley, L. K., Ingham, T., Baeza-Romero, M. T., Pöschl, U., Shiraiwa, M., Ammann, M., and Heard, D. E.: The effect of viscosity on the HO₂ uptake by sucrose and secondary organic aerosol particles, *Atmospheric Chemistry and Physics Discussions*, 1-25, 10.5194/acp-2016-284, 2016a.
- Lakey, P. S. J., George, I. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Organics Substantially Reduce HO₂ Uptake onto Aerosols Containing Transition Metal ions, *Journal of Physical Chemistry A*, 120, 1421-1430, 830 10.1021/acs.jpca.5b06316, 2016b.
- Lelieveld, J., and Crutzen, P. J.: The role of clouds in tropospheric photochemistry, *J Atmos Chem*, 12, 229-267, 10.1007/bf00048075, 1991.
- Lewis, J., Argyle, R., Bunclark, P., Evans, D., Gonzales-Solares, E., and Markwardt, C. B.: Non-linear Least Squares Fitting in IDL with MPFIT, arXiv preprint arXiv:0902.2850, 2009.
- 835 Li, H., Wang, D., Cui, L., Gao, Y., Huo, J., Wang, X., Zhang, Z., Tan, Y., Huang, Y., Cao, J., Chow, J. C., Lee, S.-c., and Fu, Q.: Characteristics of atmospheric PM_{2.5} composition during the implementation of stringent pollution control measures in Shanghai for the 2016 G20 summit, *Sci. Total Environ.*, 648, 1121-1129, 10.1016/j.scitotenv.2018.08.219, 2019a.
- Li, K., Jacob, D. J., Liao, H., Shen, L., Zhang, Q., and Bates, K. H.: Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, *Proceedings of the National Academy of Sciences*, 116, 422, 10.1073/pnas.1812168116, 2019b.
- 840 Lou, S., Liao, H., and Zhu, B.: Impacts of aerosols on surface-layer ozone concentrations in China through heterogeneous reactions and changes in photolysis rates, *Atmos. Environ.*, 85, 123-138, 10.1016/j.atmosenv.2013.12.004, 2014.
- Lundström, T., Christensen, H., and Sehested, K.: Reactions of the HO₂ radical with OH, H, Fe²⁺ and Cu²⁺ at elevated temperatures, *Radiation Physics and Chemistry*, 69, 211-216, 2004.
- Macintyre, H., and Evans, M.: Parameterisation and impact of aerosol uptake of HO₂ on a global tropospheric model, *Atmos. Chem. Phys.*, 11, 10965-10974, 2011.
- 845 Magi, L., Schweitzer, F., Pallares, C., Cherif, S., Mirabel, P., and George, C.: Investigation of the uptake rate of ozone and methyl hydroperoxide by water surfaces, *The Journal of Physical Chemistry A*, 101, 4943-4949, 1997.
- Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., St Clair, J. M., Crouse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., 850 Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaegle, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HO_x) in the Arctic troposphere in spring, *Atmos. Chem. Phys.*, 10, 5823-5838, 10.5194/acp-10-5823-2010, 2010.
- Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, *Atmos. Chem. Phys.*, 13, 509-519, 10.5194/acp-13-509-2013, 2013.
- 855 Markwardt, C. B.: Non-linear least squares fitting in IDL with MPFIT, arXiv preprint arXiv:0902.2850, 2009.
- Martin, R. V., Jacob, D. J., Yantosca, R. M., Chin, M., and Ginoux, P.: Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, *J. Geophys. Res.-Atmos.*, 108, Artn 4097, 10.1029/2002jd002622, 2003.
- Martinez, M., Harder, H., Kovacs, T. A., Simpas, J. B., Bassis, J., Leshner, R., Brune, W. H., Frost, G. J., Williams, E. J., Stroud, 860 C. A., Jobson, B. T., Roberts, J. M., Hall, S. R., Shetter, R. E., Wert, B., Fried, A., Alicke, B., Stutz, J., Young, V. L., White, A. B., and Zamora, R. J.: OH and HO₂ concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999, *J. Geophys. Res.-Atmos.*, 108, Artn 4617, 10.1029/2003jd003551, 2003.

- 865 Matthews, P. S. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Uptake of HO₂ radicals onto Arizona test dust particles using an aerosol flow tube, *Atmos. Chem. Phys.*, 14, 7397-7408, 10.5194/acp-14-7397-2014, 2014.
- Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Poschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, *Atmos. Chem. Phys.*, 9, 9491-9522, 2009.
- 870 Moon, D. R., Taverna, G. S., Anduix-Canto, C., Ingham, T., Chipperfield, M. P., Seakins, P. W., Baeza-Romero, M. T., and Heard, D. E.: Heterogeneous reaction of HO₂ with airborne TiO₂ particles and its implication for climate change mitigation strategies, *Atmos. Chem. Phys.*, 18, 327-338, 10.5194/acp-18-327-2018, 2018.
- Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G.: Mass Accommodation Coefficient for HO₂ Radicals on Aqueous Particles, *Journal of Geophysical Research-Atmospheres*, 92, 4163-4170, 1987.
- 875 Müller, B., and Heal, M. R.: The mass accommodation coefficient of ozone on an aqueous surface, *Physical Chemistry Chemical Physics*, 4, 3365-3369, 2002.
- Price, H. C., Mattsson, J., Zhang, Y., Bertram, A. K., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., and Rickards, A. M.: Water diffusion in atmospherically relevant α -pinene secondary organic material, *Chem Sci*, 6, 4876-4883, 2015.
- 880 Ross, H. B., and Noone, K. J.: A numerical investigation of the destruction of peroxy radical by Cu ion catalyzed-reactions of atmospheric particles, *J Atmos Chem*, 12, 121-136, 10.1007/bf00115775, 1991.
- Sander, R.: Modeling atmospheric chemistry: Interactions between gas-phase species and liquid cloud/aerosol particles, *Surveys in Geophysics*, 20, 1-31, 1999.
- Schwartz, S. E., and Freiberg, J. E.: Mass-transport limitation of the rate of reaction of gases in liquid droplets-application to oxidation of SO₂ in aqueous solutions, *Atmos. Environ.*, 15, 1129-1144, 10.1016/0004-6981(81)90303-6, 1981.
- 885 Schwartz, S. E.: Gas phase and aqueous phase chemistry of HO₂ in liquid water clouds, *J. Geophys. Res.-Atmos.*, 89, 1589-1598, 10.1029/JD089iD07p11589, 1984.
- Schwartz, S. E.: Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, in: *Chemistry of multiphase atmospheric systems*, Springer, 415-471, 1986.
- 890 Schwartz, S. E.: Both sides now-The chemistry of clouds, *Annals of the New York Academy of Sciences*, 502, 83-144, 10.1111/j.1749-6632.1987.tb37648.x, 1987.
- Seinfeld, J. H.: ES&T books: atmospheric chemistry and physics of air pollution, *Environ. Sci. Technol.*, 20, 863-863, 1986.
- Shiraiwa, M., Pfrang, C., and Poschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, *Atmos. Chem. Phys.*, 10, 3673-3691, 10.5194/acp-10-3673-2010, 2010.
- 895 Song, S. J., Gao, M., Xu, W. Q., Shao, J. Y., Shi, G. L., Wang, S. X., Wang, Y. X., Sun, Y. L., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, *Atmos. Chem. Phys.*, 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.
- Taketani, F., Kanaya, Y., and Akimoto, H.: Kinetics of heterogeneous reactions of HO₂ radical at ambient concentration levels with (NH₄)₂SO₄ and NaCl aerosol particles, *The Journal of Physical Chemistry A*, 112, 2370-2377, 2008.
- 900 Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous loss of HO₂ by KCl, synthetic sea salt, and natural seawater aerosol particles, *Atmos. Environ.*, 43, 1660-1665, 2009.
- Taketani, F., and Kanaya, Y.: Kinetics of HO₂ Uptake in Levoglucosan and Polystyrene Latex Particles, *J Phys Chem Lett*, 1, 1701-1704, 10.1021/jz100478s, 2010.
- Taketani, F., Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Okuzawa, K., Kawamura, K., Wang, Z., and Akimoto, H.: Measurement of overall uptake coefficients for HO₂ radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang (China), *Atmos. Chem. Phys.*, 12, 11907-11916, 10.5194/acp-12-11907-2012, 2012.
- 905 Tan, Z., Hofzumahaus, A., Lu, K., Brown, S. S., Holland, F., Huey, L. G., Kiendler-Scharr, A., Li, X., Liu, X., and Ma, N.: No Evidence for a Significant Impact of Heterogeneous Chemistry on Radical Concentrations in the North China Plain in Summer 2014, *Environ. Sci. Technol.*, 2020.
- 910 Tan, Z. F., Fuchs, H., Lu, K. D., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H. B., Gomm, S., Haseler, R., He, L. Y., Holland, F., Li, X., Liu, Y., Lu, S. H., Rohrer, F., Shao, M., Wang, B. L., Wang, M., Wu, Y. S., Zeng, L. M., Zhang, Y. S., Wahner, A., and Zhang, Y. H.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO₂ and RO₂ radicals, *Atmos. Chem. Phys.*, 17, 663-690, 10.5194/acp-17-663-2017, 2017.

- 915 Tang, M. J., Huang, X., Lu, K. D., Ge, M. F., Li, Y. J., Cheng, P., Zhu, T., Ding, A. J., Zhang, Y. H., Gligorovski, S., Song, W., Ding, X., Bi, X. H., and Wang, X. M.: Heterogeneous reactions of mineral dust aerosol: implications for tropospheric oxidation capacity, *Atmos. Chem. Phys.*, 17, 11727-11777, 10.5194/acp-17-11727-2017, 2017.
- Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning PM_{2.5} chemical composition, aerosol optical properties and their relationships across China, *Atmos. Chem. Phys.*, 17, 9485, 2017.
- 920 Thornton, J., and Abbatt, J. P. D.: Measurements of HO₂ uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, *Journal of Geophysical Research: Atmospheres*, 110, 10.1029/2004JD005402, 2005a.
- Thornton, J., and Abbatt, J. P. D.: Measurements of HO₂ uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, *J. Geophys. Res.-Atmos.*, 110, 10.1029/2004jd005402, 2005b.
- Thornton, J. A., Jaegle, L., and McNeill, V. F.: Assessing known pathways for HO₂ loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, *Journal of Geophysical Research: Atmospheres*, 113, 2008.
- 925 Tie, X., Brasseur, G., Emmons, L., Horowitz, L., and Kinnison, D.: Effects of aerosols on tropospheric oxidants: A global model study, *J. Geophys. Res.-Atmos.*, 106, 22931-22964, Doi 10.1029/2001jd900206, 2001.
- Utter, R. G., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of the mass accommodation coefficient of ozone on aqueous surfaces, *J Phys Chem-Us*, 96, 4973-4979, 10.1021/j100191a045, 1992.
- 930 Whalley, L. K., Furneaux, K. L., Goddard, A., Lee, J. D., Mahajan, A., Oetjen, H., Read, K. A., Kaaden, N., Carpenter, L. J., Lewis, A. C., Plane, J. M. C., Saltzman, E. S., Wiedensohler, A., and Heard, D. E.: The chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic Ocean, *Atmos. Chem. Phys.*, 10, 1555-1576, 10.5194/acp-10-1555-2010, 2010.
- Whalley, L. K., Stone, D., George, I. J., Mertes, S., van Pinxteren, D., Tilgner, A., Herrmann, H., Evans, M. J., and Heard, D. E.: The influence of clouds on radical concentrations: observations and modelling studies of HO_x during the Hill Cap Cloud Thuringia (HCCT) campaign in 2010, *Atmos. Chem. Phys.*, 15, 3289-3301, 10.5194/acp-15-3289-2015, 2015.
- 935 Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, *Atmos. Chem. Phys.*, 14, 13175-13188, 10.5194/acp-14-13175-2014, 2014.
- Yin, J., Allen, A. G., Harrison, R. M., Jennings, S. G., Wright, E., Fitzpatrick, M., Healy, T., Barry, E., Ceburnis, D., and McCusker, D.: Major component composition of urban PM₁₀ and PM_{2.5} in Ireland, *Atmos. Res.*, 78, 149-165, <https://doi.org/10.1016/j.atmosres.2005.03.006>, 2005.
- 940 Zou, Q., Song, H., Tang, M., and Lu, K.: Measurements of HO₂ uptake coefficient on aqueous (NH₄)₂SO₄ aerosol using aerosol flow tube with LIF system, *Chinese Chemical Letters*, <https://doi.org/10.1016/j.ccllet.2019.07.041>, 2019.