

## Response to the comments of referee #2

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

We have now added D. Moon, M. Baeza-Romero and D. Heard as co-authors to this paper since their unpublished experimental data have been included in this paper and they have contributed to enhance the manuscript.

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

- 1 The comparison of the results from the empirical equation proposed here with the existing parameterization proposed by IUPAC.
- 2 Discussion of the influence of the organic content of particles.
- 3 Correction of different definitions of the same terms and the obscure statements.
- 4 The corrections of citations in the manuscript.
- 5 Responses to other specific points.
- 6 Explanation of part of the SI

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

The manuscript of Song et al deals with an important theme in atmospheric science; the interaction of HO<sub>2</sub> with particles containing dissolved copper and the modelling of the impact of this heterogeneous reaction on e.g. O<sub>3</sub> production.

We thank the reviewer for recognising this.

1.1 Song et al have analysed laboratory data and derived an empirical expression that they then implemented in a model. They suggest that their parameterisation is superior to taking a constant value of 0.2 for the uptake coefficient. This is most likely true but why do they not compare to other parameterisations of this process, e.g. that proposed by IUPAC which also considers laboratory studies up to 2016 and which has a physical basis (i.e. aqueous phase rate coefficients for reaction of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> with Cu).

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

2.1 They also do not consider in any detail the potential for organic content of particles to reduce the uptake coefficient considerably as this is mentioned only in passing on line 312-315. Thus aspect

will be central to improving the modelling of HO<sub>2</sub> uptake to particle matter, as has been shown e.g. for N<sub>2</sub>O<sub>5</sub>. The sentence on line 149-150 in this regard is highly misleading: “Without the interference of organic matter, it is convenient to explore the mechanism of HO<sub>2</sub> heterogeneous uptake and derive its parameterized equation, which provides a good reference for the heterogeneous uptake of HO<sub>2</sub> in the actual atmosphere environment”. The co-authors from Jülich will be intimately familiar with this aspect of heterogeneous chemistry and should be able to provide input.

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

“A simplified approach was used to explore the mechanism of HO<sub>2</sub> heterogeneous uptake in order to derive a parameterized equation for the uptake coefficient,  $\gamma_{HO_2}$ , and which did not consider any potential role of organic matter present in the aerosol because of the reasons detailed below.

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

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

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

Abstract

1 Introduction

2 Materials and Methods

2.1 The Model

2.2 Corrections on  $\gamma_{HO_2}$  in the MARK model

2.2.1 Henry’s law of gas phase reactants

2.2.2 Aerosol particle condensed phase Cu<sup>2+</sup> molality calculation

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

2.3 Laboratory results for the HO<sub>2</sub> accommodation coefficient

3 Results and Discussion

- 3.1 Parameter sensitivity analysis of the MARK model
- 3.2 Model Validation
- 3.3 A novel parameterized equation of  $\gamma_{HO_2}$
- 3.4 Evaluation of the impact of the new HO<sub>2</sub> uptake parametrization in the Wangdu campaign
  - 3.4.1 Average results of observed meteorological parameters and trace gases concentration in Wangdu campaign
  - 3.4.2 Calculation of soluble copper ion concentration
  - 3.4.3  $\gamma_{HO_2}$  estimated at Wangdu field campaign
- 4 Summary and conclusions
- Author Contribution
- Competing Interest
- Data Availability
- Acknowledgments
- References

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

- S1 Reaction mechanism and reaction rate constants
  - S2 Calculation of aerosol liquid water content (ALWC) and other important parameters for conditions encountered during the Wangdu campaign
  - S3 The uncertainty of the calculation for conditions encountered during the Wangdu campaign
- We also added the forward and backward reaction rate constants in Table S. 2 in the MARK model calculation.
- Please see the SI for more details.

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

In response to the Short Comment from Professor D. Heard, and in consultation with the Leeds group, we have modified the way the data are presented in the Table and Figure (there were some mistakes and incorrect citations were used). The citations in the revised MS have been corrected based on the short comment of Professor D. Heard (please see also the response to the first short comment).

Some specific points are listed below:

- 3.2 L11 hydroxyl peroxy radicals = hydroperoxyl radicals  
L12 gamma\_HO2 is defined but the expression after line 17 simply lists gamma.  
In the new version it has been taken care that only “hydroperoxyl radicals” is used. We changed the wording in the abstract and line 34 in the Introduction.
- 3.3 L15 parameterisation of HO<sub>2</sub>? Presumably of HO<sub>2</sub> uptake  
On line 21 in the Abstract we have added the word “uptake” in the revised MS.
- 3.4 Does it make sense to list the expression in the abstract, where none of the terms (e.g. ALWC,

[PM], Rd) involved are defined

We changed the abstract in the revised MS including the definition of the main parameters of the parametrization as follows:

“Heterogeneous uptake of hydroperoxyl radicals (HO<sub>2</sub>) onto aerosols has been proposed to be a significant sink of HOx and hence the atmospheric oxidation capacity. Accurate calculation of the HO<sub>2</sub> uptake coefficient  $\gamma_{HO_2}$  is key to quantifying the potential impact of this atmospheric process. Laboratory studies show that  $\gamma_{HO_2}$  can vary by orders of magnitude due to changes in aerosol properties, especially aerosol soluble copper (Cu) and aerosol liquid water content (ALWC). In this study we present a state-of-the-art model to simulate both gas and aerosol phase chemistry for the uptake of HO<sub>2</sub> onto Cu-doped aerosols. Moreover, a novel parameterization of HO<sub>2</sub> uptake was developed that considers changes in relative humidity (RH) and condensed phase Cu ion concentrations and which is based on a model optimization using previously published laboratory and new laboratory data included in this workdata. The new parameterization is as follows:

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

where  $\alpha$  is the mass accommodation coefficients which is the probability that a gas-phase molecule colliding with the aerosol surface leads to dissolution, reaction or volatilization,  $v_{HO_2}$  is the mean molecular speed of HO<sub>2</sub> [cm s<sup>-1</sup>],  $R_d$  is the Count Median Radius of the aerosols [cm],  $H_{corr}$  is the Henry's constant [mol cm<sup>-3</sup> atm<sup>-1</sup>] corrected by solution pH ( $H_{corr} = H_0 \times \left(1 + \frac{K_{eq}}{[H^+]}\right)$ , where  $H_0$  is the physical Henry's law constant),  $R$  is the gas constant [cm<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup>],  $T$  is the temperature [K] and [PM] is the mass concentration of particles [μg m<sup>-3</sup>]. According to the new equation, highly variable HO<sub>2</sub> uptake coefficients (median value ~0.1) were obtained for the North China Plain and the impact of HO<sub>2</sub> uptake on the ROx (=OH + HO<sub>2</sub> + RO<sub>2</sub>) budget was assessed.”

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

We mean that the role of the reduction of HO<sub>2</sub> uptake on aerosol toward that of O<sub>3</sub> production is also dependent on the selection of the HO<sub>2</sub> uptake coefficient, as well as the reduction of aerosol mass itself. We try to modify the text to become clearer as follows,

“... the reduced HO<sub>2</sub> 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  $\gamma_{HO_2}$ .”

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

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

3.7 L68 MARKM model is otherwise referred to as MARK

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

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

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

3.9 L/3  $H_0$  is estimated (Thornton et al, 2008) to be 3900 M atm<sup>-1</sup>. Why is this cited in different units to the effective solubility ( $H^{cc}$ ). How good is this “estimate” and on what data is it based (I believe Hanson 1992, who also lists a T-dependence)?

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

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

At 298K,  $H_0$  equals to 3897.13 M atm<sup>-1</sup> calculated from the formula, and the estimation as 3900 M atm<sup>-1</sup> may cause small deviation.

We changed the equation 4 in the revised MS as:

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

In our model, the T-dependence formula is used in the MARK model now. No difference between the original and revised results have been shown because at 298K, with the T dependent parametrization a value of 3897.13 M atm<sup>-1</sup> is obtained for  $H_0$  while a value of 3900 was used before.

3.10 L101 Define  $[x_i]_{equ}$ . In the line above only  $[x_i]$  is mentioned.

In the bulk condensed phase of aerosol particle, the effective concentration  $[x_i]_{equ}$ , rather than total concentration of ions, should be calculated because of the high ionic strength. We added “effective” to the original sentence under the equation (9) in the revised MS and show the equation of effective  $[Cu^{2+}]_{equ}$  in the aerosol particle condensed phase as Equation (11).

5.1 L105 “steady-state” HO<sub>2</sub> concentration. Why “steady-state”?

As discussed below (please see response to Comment 1.5), the parameterization proposed by IUPAC is originally from the heterogeneous modeling with liquid droplets and modified by the Resistance Model (Danckwerts, 1951; Schwartz, 1984; Schwartz, 1986; Ammann et al., 2013; Davidovits et al., 2006). The Resistance Model is based on the assumption of steady-state solutions (liquid water cloud droplets). The novel parameterization proposed by Song et al. is still built on the basic framework of the Resistance model, thus only steady-state HO<sub>2</sub> concentration can be calculated and in consequence this novel parameterization has the limitation of steady-state assumption.

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

3.11 L110  $k_{eff}$  is listed in the equation 11. This appears to be defined 57 lines later, but not always in the same manner.

We defined  $k_{eff}$  as “the comprehensive reaction rate coefficient encompasses both HO<sub>2</sub> dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO<sub>2</sub> uptake

process.” on line 147 just under the Equation (13) in Section 2.2.3 of the revised MS. This is the place where the definition first appeared. We deleted the conflict definitions below.

3.12 Tab1 (and abstract) the accommodation coefficient is not defined, as far as I can see. We have added the definitions of relevant parameters of the parameterization in the revised MS Abstract. Please see response to comment 3.4.

5.2 Tab1 The data of Lakey 2015/2016 and Zou 2019 are not mentioned (Moon = Lakey ???) Following consultation with the Leeds group, we added the published data by Lakey et al. 2016 and Zou et al. 2019 in the revised MS Table 1.

The study of Lakey et al, 2015 measured  $\gamma_{HO_2}$  on single component organic aerosols and the Cu ion concentration was not high enough ( $\sim 0.7\text{--}1.3 \times 10^{-6}$  to  $5.5 \times 10^{-4}$  M) to measure  $\alpha$ . Thus, we did not include the data from Lakey (2015) in the Table 1. The citations used in the original MS are corrected based on the Short Comment to this paper from Prof. D. Heard and the response to that. Please see the response to the first short comment.

Table 1:  $\gamma_{HO_2}$  under lab conditions for Cu<sup>2+</sup>-doped inorganic aerosols.

Aerosol type	RH/%	Estimation of [Cu] in aerosol/M	$\alpha_{HO_2}$	Ref.
NH <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	75%	0.0059–0.067*	0.40±0.21	(Mozurkewich et al., 1987)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	45%	0.5	0.53±0.13	(Taketani et al., 2008)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	42%	0.16	0.5±0.1	(Thornton and Abbatt, 2005)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	53–65%	0.5–0.7*	0.4±0.3	(George et al., 2013)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	65%	0.57	0.26±0.02	(Lakey et al., 2016)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	51%	0.0027	0.096±0.024	(Zou et al., 2019)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	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 <sub>3</sub>	75%	0.03–0.0063*	0.94±0.5	(Mozurkewich et al., 1987)

\*Cu concentration is in molality (mol kg<sup>-1</sup>).

3.13 Tab2 Add units, do not capitalize K...

Table 2 is moved to the Supplemental Information of the revised MS as Table S.1. In Table S.1 we add the units of reaction rate constants as: “k<sub>298</sub>/M<sup>n</sup> s<sup>-1</sup>” in the header.

6.1 ...and move to supplementary information

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

3.14 Tab3 K should be capitalized (eqm.)

We changed to a capital K<sub>298</sub>.

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

It does not refer to a global average. It is the annual average contribution across China based on the

research of Tao et al., (Tao et al., 2017). We added “across China” in the original statement on line 173 as: “...contribution of inorganic aerosol to PM<sub>2.5</sub> is between 25% and 48% across China (Tao et al., 2017).”

5.3 Fig1 Please explain why the uptake coefficient continues to increase at pH > 5 whereas  $k_{eff}$  decreases.

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

In the revised MS, we deleted the original  $k_{eff}$  graph (Figure 1) to avoid confusion in the understanding of the entire reaction system, and we have included the quasi-first order reaction rate constant  $k_{het}$  of the gas phase HO<sub>2</sub> as in the new Figure 1.

Figure 1 and the explanation are corrected as follows in the revised MS:

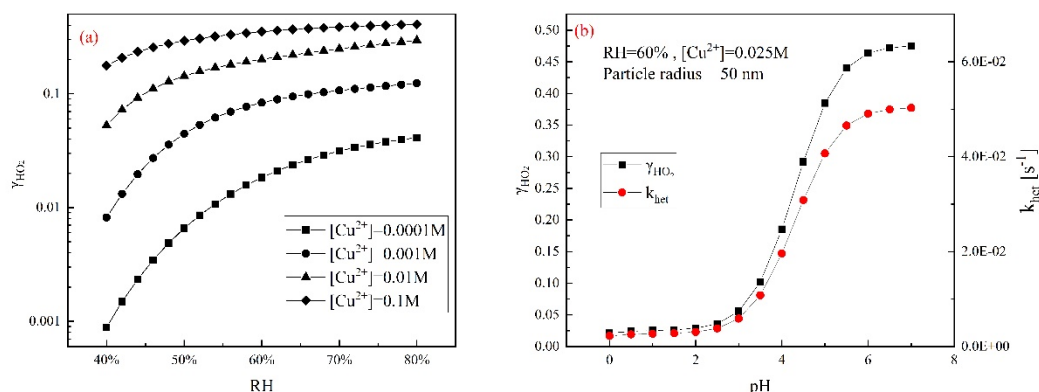


Figure 1: Influence of various parameters upon  $\gamma_{HO_2}$  predicted by the MARK model. (a)  $\gamma_{HO_2}$  increases with the RH at different [Cu<sup>2+</sup>]; (b)  $\gamma_{HO_2}$  denoted by black squares and black line and  $k_{het}$  in red circles and red line increase with aerosol particle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

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

“ $\gamma_{HO_2}$  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<sub>2</sub> 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<sub>2</sub>. This trend is consistent with the observed second-order rate constant of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> reviewed by Bielski et al. 1985 (Bielski et al., 1985). Moreover, aqueous phase reaction rates of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> and Cu<sup>2+</sup>/Cu<sup>+</sup> increase with the increasing of condensed phase pH because in alkaline environment HO<sub>2</sub> is more likely becoming O<sub>2</sub><sup>-</sup> which has quicker reaction rate with Cu<sup>2+</sup>/Cu<sup>+</sup>. The pH of the ambient atmospheric aerosol is measured

generally below 5 even when the concentration of  $\text{NH}_3$  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,  $\gamma_{\text{HO}_2}$  is highly affected by aerosol condensed phase pH may mainly because of the change of solubility.”

3.16 L166  $k_{\text{eff}}$  is defined as a comprehensive reaction rate constant. . . . during heterogeneous uptake. On L210,  $K_{\text{eff}}$  is defined as the rate of  $\text{HO}_2$  aqueous reaction with copper ions.

Please see response to Comment 3.11 above.

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

Please see the response to Comment 1.1.

1.3 L180 Based on the data of Lakey et al, IUPAC list a rate coefficient for  $\text{HO}_2$  ( $\text{O}_2^-$ ) with Cu ions of  $5 \times 10^5$ . This is orders of magnitude lower than those listed.

We added the following explanation in Section 3.2 the last paragraph of the revised MS on line 245: “There is more discussion about this reaction rate. IUPAC (Ammann et al., 2013; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.) proposed the effective rate coefficient for the reaction of  $\text{HO}_2$  ( $\text{O}_2^-$ ) 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; Huie, 2003), the rate coefficient of  $\text{HO}_2$  with  $\text{Cu}^{2+}$  is  $1 \times 10^8$  or  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at  $\text{pH}=2$  and  $\text{pH}=1$ , respectively. These two rate coefficients were quantified in a low pH environment ( $\text{pH}=2$  for  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $\text{pH}=1$  for  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). At the same time, the reaction rate of  $\text{O}_2^-$  with  $\text{Cu}^{2+}$  is  $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for pH in the range 3-6.5 (Huie, 2003). At higher pH, the reaction rate of  $\text{HO}_2$  with  $\text{Cu}^{2+}$  may change, but it is unknown whether it will decrease by four orders of magnitude. Further kinetics experiments are needed at varying pH to verify the reaction rate coefficient of  $\text{Cu}^{2+}$  ions with  $\text{HO}_2$  and  $\text{O}_2^-$  in aqueous solution.”

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

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

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

The focus of this manuscript is to investigate the influence of copper ions on  $\text{HO}_2$  heterogeneous reactions and it proposes a new empirical parameterisation applicable to ambient copper ion containing aerosols. Therefore, we only included the experimental results of Taketani et al. obtained with copper-doped inorganic aerosols and did not include other experimental studies of inorganic aerosol not doped with copper ions, which are inconsistent with other measurements, perhaps owing to differences in experimental conditions in the laboratory (George et al., 2013) as follows. The mechanism of  $\text{HO}_2$  uptake with single component aerosols (such as  $(\text{NH}_4)_2\text{SO}_4$ ) is still not fully understood. Moreover,  $\text{HO}_2$  uptake coefficient measurement is highly affected by experimental



conditions such as HO<sub>2</sub> concentration, reaction time, etc. Some data from Taketani et al. are not consistent with other measurements within the community. Taketani reported  $\gamma_{HO_2} = 0.11 \pm 0.03$  at 45% RH,  $0.15 \pm 0.03$  at 55% RH,  $0.17 \pm 0.04$  at 65% RH and  $0.19 \pm 0.04$  at 75% RH when the HO<sub>2</sub> initial concentration was  $1 \times 10^8$  molecule cm<sup>-3</sup>, which are inconsistent with results from Thornton and Abbatt. Thornton and Abbatt concluded that the  $\gamma$  for wet particles of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is  $< 0.01$  at ~42% RH and a HO<sub>2</sub> ambient concentration of  $\sim 1 \times 10^8$  molecule cm<sup>-3</sup> from extrapolation based on their research with HO<sub>2</sub> initial concentration at  $5 \times 10^{10}$  molecule cm<sup>-3</sup>. George et al. (2013) reported  $\gamma_{HO_2}$  as  $0.003 \pm 0.005$  at 55% RH and  $0.01 \pm 0.01$  at 65-75% RH at HO<sub>2</sub> initial concentration of  $1.5 \times 10^8$  -  $1.5 \times 10^9$ , also much lower than the measurements of Taketani et al. The initial HO<sub>2</sub> concentration and Cu<sup>2+</sup> contamination will also affect  $\gamma_{HO_2}$ .

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

Please see the response to Comment 1.1.

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

Please see the response to Comment 1.3 above. We agree with the referee, that the IUPAC parameterization reproduces the laboratory studies from Lakey et al. with  $k_{TMI}$  (defined as the second order rate coefficient for the reaction of HO<sub>2</sub> /O<sub>2</sub><sup>-</sup> with transition metal ions) equal to  $5 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>. However, we also note that IUPAC states “the parameterization suggested here is very sensitive to the solubility of HO<sub>2</sub> ( $H_{HO_2}$ ), its temperature dependence and on the aerosol pH”, which we attempt to address in our new parameterisation.

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

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

The definition of  $\gamma_{HO_2}$  is from the Appendix A of Hanson et al., 1994 (Hanson et al., 1994). We add the citation on line 270 in Section 3.3 second paragraph as: “Hanson et al. (1994) proposed the

definition of the uptake coefficient as  $\gamma = \alpha \left( 1 - \frac{c_{a,surf}}{H^{cc} c_{g,surf}} \right)$  where  $c_{a,surf}$  is the surface

concentration of the reactant,  $c_{g,surf}$  is the gas phase concentration. In the process of HO<sub>2</sub> uptake, we deduce the parameterized equation of  $\gamma_{HO_2}$  in the framework of the resistance model.”

6.2 L265 section 3.4.2. could be move to SI

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

We move section 3.4.2. to the SI.

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

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

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

Please see the response to Comment 2.1.

6.3 L351 move section 3.4.5 to SI

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

We move section 3.4.5 to the SI.

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

Bielski, B. H., Cabelli, D. E., Arudi, R. L., and Ross, A. B.: Reactivity of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radicals in aqueous solution., *Journal of physical and chemical reference data*, 14, 1041-1100, 1985.

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

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

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

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 HO<sub>2</sub> 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-Hd<sub>0</sub>) for H-OH, H-OOH, H-OO-, H-O., H-OO-, and H-OO, *J Phys Chem-Us*, 94, 5413-5415, 10.1021/j100376a046, 1990.

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

Hanson, D. R., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of OH and HO<sub>2</sub> radical uptake coefficients on water and sulfuric-acid surfaces, *J Phys Chem-Us*, 96, 4979-4985, Doi 10.1021/J100191a046, 1992.

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

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.

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.

Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO<sub>2</sub> Uptake Coefficients onto Single Component Organic Aerosols, *Environ. Sci. Technol.*, 49, 4878-4885, 10.1021/acs.est.5b00948, 2015.

Lakey, P. S. J., George, I. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Organics Substantially Reduce HO<sub>2</sub> Uptake onto Aerosols Containing Transition Metal ions, *Journal of Physical Chemistry A*, 120, 1421-1430, 10.1021/acs.jpca.5b06316, 2016.

Lundström, T., Christensen, H., and Sehested, K.: Reactions of the HO<sub>2</sub> radical with OH, H, Fe<sup>2+</sup> and Cu<sup>2+</sup> at elevated temperatures, *Radiation Physics and Chemistry*, 69, 211-216, 2004.

Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G.: Mass Accommodation Coefficient for HO<sub>2</sub> Radicals on Aqueous Particles, *Journal of Geophysical Research-Atmospheres*, 92, 4163-4170, 1987.

Schwartz, S. E.: Gas phase and aqueous phase chemistry of HO<sub>2</sub> 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.

Taketani, F., Kanaya, Y., and Akimoto, H.: Kinetics of heterogeneous reactions of HO<sub>2</sub> radical at ambient concentration levels with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NaCl aerosol particles, *The Journal of Physical Chemistry A*, 112, 2370-2377, 2008.

Taketani, F., Kanaya, Y., and Akimoto, H.: Heterogeneous loss of HO<sub>2</sub> by KCl, synthetic sea salt, and natural seawater aerosol particles, *Atmos. Environ.*, 43, 1660-1665, 2009.

Tao, J., Zhang, L., Cao, J., and Zhang, R.: A review of current knowledge concerning PM<sub>2.5</sub> chemical composition, aerosol optical properties and their relationships across China, *Atmos. Chem. Phys.*, 17, 9485, 2017.

Thornton, J., and Abbatt, J. P. D.: Measurements of HO<sub>2</sub> uptake to aqueous aerosol: Mass accommodation coefficients and net reactive loss, *J. Geophys. Res.-Atmos.*, 110, 10.1029/2004jd005402, 2005.

Thornton, J. A., Jaegle, L., and McNeill, V. F.: Assessing known pathways for HO<sub>2</sub> loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, *Journal of Geophysical Research: Atmospheres*, 113, 2008.

Zhou, J., Murano, K., Kohno, N., Sakamoto, Y., and Kajii, Y.: Real-time quantification of the total HO<sub>2</sub> reactivity of ambient air and HO<sub>2</sub> uptake kinetics onto ambient aerosols in Kyoto (Japan), *Atmos. Environ.*, 223, 117189, <https://doi.org/10.1016/j.atmosenv.2019.117189>, 2020.

Zou, Q., Song, H., Tang, M., and Lu, K.: Measurements of HO<sub>2</sub> uptake coefficient on aqueous (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol using aerosol flow tube with LIF system, *Chinese Chemical Letters*, <https://doi.org/10.1016/j.ccl.2019.07.041>, 2019.

