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

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Abstract. The heterogeneous uptake of hydroxyl peroxy radicals (HO₂) on aerosol has been proposed to be a significant sink of HOx, thus could influence the atmospheric oxidation capacity. Accurate calculation of the uptake coefficient γ_{HO_2} is the key to quantifying its atmospheric effects. Laboratory studies show that γ_{HO_2} varies by orders of magnitude due to change in aerosol properties, especially those of aerosol soluble copper (Cu) and aerosol liquid water content (ALWC). In this study,

15 we develop a state-of-the-art model to simulate both gas and aerosol phase chemistry. A novel parameterized equation of HO₂ considering change in RH and aerosol Cu is developed based on model optimization toward all available lab experiments.

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

According to the new equation, highly variable HO₂ uptake coefficients (median value~0.1) were diagnosed for North China

20 Plain and the impact of HO₂ uptake on the ROx budget is assessed.

1 Introduction

The atmospheric cleansing capacity of the troposphere is largely determined by the concentrations of the hydroxyl radical, which are closely linked with the concentrations of the hydroxyl peroxy (HO₂) radical. In the established chemical

25 mechanism, the coupling of OH and HO₂ is strongly determined by the reaction of OH + VOCs/CO/HCHO/CH₄/H₂/SO₂ and HO₂ + 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 HO₂ under some conditions such as low NO(Tang et al., 2017). For high aerosol mass load, the reaction rate of HO₂ with aerosol particles could be fast enough to influence the concentration of HOx radicals, and consequently, reduce ozone production from HO₂+NO(Kanaya et al., 2009;Li et al.,

30 2019b).

From a global perspective, the impact of HO$_2$ uptake on the calculated HOx concentrations is diagnosed to be about 10~40 %(Jacob, 2000;Whalley et al., 2015;Whalley et al., 2010;Mao et al., 2010;Li et al., 2019b;Li et al., 2019a) when γ_{HO2} (heterogeneous uptake coefficient(Schwartz and Meyer, 1986)) is assumed to be 0.2(Tie et al., 2001;Martin et al., 2003). The diagnosed impact of HO$_2$ uptake is lowered when using a parameterized equation of γ_{HO_2} without considering the influence

35 of transition metal ions (TMIs)(Thornton et al., 2008), and still, a significant impact on the calculated [OH] and O$_3$ production rate aresuggested 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 impact on the simulated HO$_2$ concentrations and local O$_3$ production rates in Chinese urban regions: Beijing, Shanghai, and Guangzhou. Furthermore, researchers have pointed out that in the North China Plain(Li et al., 2019a;Li et al., 2019b), the reduced of HO$_2$ uptake on aerosol is a key reason for the

40 increase in surface ozone over the last few years due to the suppression of NOx lifetime with γ_{HO_2} fixed at 0.2.

Previous studies show that γ_{HO_2} from the laboratory, field, and modeling studies span several orders of magnitude, ranging from <0.002 for dry aerosols(Cooper and Abbatt, 1996;Taketani et al., 2008a) to 0.2 for neutralized aerosols(Thornton and Abbatt, 2005). Much higher values of γ_{HO_2} have been measured and calculated for Cu-doped aerosols(Mozurkewich et al., 1987;Taketani et al., 2008b;Thornton and Abbatt, 2005;Thornton et al., 2008;Cooper and Abbatt, 1996). For fine particles,

45 the reactions of HO$_2$ with soluble Cu ions may be fast enough to be limited by the accommodation coefficient α. Due to the widespread distribution of Cu^{2+} in ambient particles, an accurate evaluation of γ_{HO_2} is one of the largest uncertainties for the determination of the impact of HO$_2$ uptake on worrisome and pressing atmospheric issues such as ozone formation.

In this study, we reanalyzed various results on the aerosol uptake of HO$_2$ from both laboratory and field studies reported in literature and propose a novel parameterized equation for the prediction of γ_{HO_2} that best fits all the lab results. Furthermore,

50 for a field campaign, we also calculated γ_{HO_2} according to the novel parameterized equation and the impact of HO$_2$ uptake on HOx budget were evaluated.

2 Materials and Methods

2.1 The Model

A Multiphase Reaction Kinetic Model (MARK) is developed in this study for the simulation of γ_{HO_2} for both the lab and

55 field experiments. The MARK model is currently capable of simulating inorganic deliquescent aerosol at ambient pressure and temperature. The model directly calculates the net gas phase uptake loss rate, k_{het}, in Eq. (1). In this model, aerosol liquid water content (L)[g cm^{-3}] is more pertinent than surface density because of the influence of the RH on uptake process(Kuang et al., 2018;Bian et al., 2014).

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

60 $$k_{het} = \left(\frac{r_p}{D_g} + \frac{4}{\gamma \bar{v}}\right)^{-1} \times \frac{3L}{r_p} \tag{2}$$

where r_p is the aerosol particle radius[cm], $\bar{v}$ is the mean molecular speed of HO$_2$ [cm s^{-1}]. and D_g is the gas phase diffusion coefficient [cm^{2}s^{-1}]. The units of aqueous reagents are converted to molecules cm^{-3}. Aerosol particle bulk phase is not an ideal solution in which an effective Henry's law constant H^{cc} should be applied in the model calculation, considering the effects of solution pH and the "*salting out*" effect of HO$_2$ and other gas reactants(Ross and Noone, 1991). This study uses the ISORROPIA II thermodynamic model(Fountoukis and Nenes, 2007) to calculate the properties of metastable deliquescent aerosols. The effective Cu^{2+} concentration in the aqueous phase, which is strongly influenced by non-ideal solution ionic strength, is also calculated following Ross and Noone(Ross and Noone, 1991).

2.2 Corrections on γ_{HO_2} in MARKM model

2.2.1 Henry's law of gas phase reactants

Aerosol bulk phase solution is not an ideal solution. The addition of an electrolyte to water interferes with the gas dissolution and the organization of water around the gas. This frequently results in a decrease in the solubility, or a "salting out" effect. This salting out effect is frequently a linear function of the molar ionic strength I. H^{cc} is the effective Henry's law constant of HO$_2$[mol cm^{-3} atm^{-1}], H_0 is the physical Henry's law constant, estimated to be about 3900 M atm^{-1} at 298K(Thornton et al., 2008). k_{eq} is the solution equilibrium constant for HO$_2$ in the gas phase. Activity coefficient A for HO$_2$ and other neutral small molecule can be expressed as(Ross and Noone, 1991):

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

$$A_{HO_2} = 10^{-0.1 \times I} \tag{4}$$

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

2.2.2 Aerosol bulk phase Cu molality calculation

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

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

Based on Ross and Noone(Ross and Noone, 1991), for an ion (Xi) of charge zi, the activity coefficient (φx) is

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

$$D = \frac{0.5109\sqrt{I}}{1+1.5\sqrt{I}} \tag{6}$$

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

95 $\quad$ $$I = \frac{1}{2} \cdot \sum m_i \cdot z_i^2 \tag{7}$$

$\varepsilon(x,y,I)$ is referred to as "interaction coefficients", and the summation extends over all ions (y) in the solution at a molality of m_y. For ions of similar charge, ε is set to zero. For ions of unequal charge, ε may be calculated from the mean activity coefficient $log(A_\pm)$ (Clegg et al., 1998) of the single electrolyte ($log(A_\pm)$) at the same I where

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

100 $\quad$ In the bulk of aerosol particle, the molality of an ion x_i can be calculated as

$$[x_i]_{equ} = [x_i] \times \varphi x \tag{9}$$

In aerosol bulk phase, effective concentration rather than total concentration of Cu ion should be calculated in HO$_2$ catalytic aqueous reaction. The effective concentration of Cu ion can be calculated as $[Cu^{2+}] \times \varphi_{Cu^{2+}}$.

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

105 $\quad$ Gas phase HO$_2$ molecules dissolve in the bulk phase and diffuse from the surface of a particle toward the center coupled with aqueous phase reactions. We need to evaluate $[\overline{HO_2}]$, the assumed averaged steady-state HO$_2$ concentration over the volume of particle. $[HO_{2(r)}]$ is HO$_2$ concentration at the surface. The ratio of these two concentration can be calculated as(Schwartz and Meyer, 1986):

$$\frac{[\overline{HO_2}]}{[HO_{2(r)}]} = 3 \times (\frac{coth(q)}{q} - \frac{1}{q^2}) \tag{10}$$

110 $\quad$ $$q = r_p \times (\frac{k_{eff}}{D_{aq}})^{0.5} \tag{11}$$

Where the r$_p$ means the geometer mean radius of the particle[cm], D_{aq} is the aqueous phase diffusion coefficient [cm^{2}s^{-1}]. In the copper-doped aerosol particle, because of the high value of k_{eff} and small equivalent particle radius (usually smaller than 250nm), the ratio is approximately equal to 1 (higher than 0.95 at 200nm diameter particle based on the calculation) . Thus, in this model, we assume the surface concentration of HO$_2$ equals to the bulk phase average HO$_2$ concentration.

2.3 Laboratory results for the HO₂ accommodation coefficient

The accommodation coefficient of HO$_2$ was determined for copper-doped inorganic aerosol in various previous lab studies. The accommodation coefficient α is approximately 0.5 in sulfate aerosol and even higher for chlorine or nitrate aerosol

because of the catalysis effect of Cu^{2+} on aqueous HO_2/ O_2^- (Table 1). In this situation, the aqueous reactions are fast enough that the uptake process is limited primarily by the mass transport process (accommodation).

120   With the wide distribution of Cu(II) in aerosol particles, a high accommodation coefficient of HO_2 presents the possibility of HO_2 uptake as an important sink of the HOx radical. According to existing research results, the model typically selects the accommodation coefficient α as 0.5.

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

Aerosol type	RH/%	Estimation of [Cu] in aerosol/M	α	Ref.
NH_4HSO_4	75%	0.0059~0.067	0.40±0.21	Mozurkewich et al.(Mozurkewich et al., 1987)
$(NH_4)_2SO_4$	45%	0.38	0.53±0.12	Taketani et al.(Taketani et al., 2008b)
$(NH_4)_2SO_4$	42%	0.16	0.5±0.1	Thornton and Abbatt(Thornton and Abbatt, 2005)
$(NH_4)_2SO_4$	55%	0.34	0.5±0.3	Moon(Moon et al., 2018)
$(NH_4)_2SO_4$	53~65%	0.5~0.7	0.4±0.2	George et al.(George et al., 2013)
NaCl	53%	~0.5	0.65±0.17	Taketani et al.(Taketani et al., 2008b)
KCl	75%	5% of KCl solution	0.55±0.19	Taketani et al.(Taketani et al., 2009)
$LiNO_3$	75%	0.03~0.063	0.94±0.5	Mozurkewich et al.(Mozurkewich et al., 1987)

125   **2.4 Reaction mechanism and reaction rate constant**

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

130   summarized below.

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

No.	Reactions	K_{298}	E_a
R1	$Cu^+ + HO_{2(aq)} \rightarrow Cu^{2+} + H_2O_{2(aq)}$	2.2×10^9	
R2	$Cu^+ + 2H^+ + O_2^- \rightarrow Cu^{2+} + H_2O_{2(aq)}$	9.4×10^9	
R3	$Cu^+ + OH_{(aq)} \rightarrow Cu^{2+} + H_2O_{2(aq)}$	3×10^9	
R4	$Cu^+ + O_{2(aq)} \rightarrow Cu^{2+} + O_2^-$	4.6×10^5	
R5	$Cu^+ + H^+ + O_{3(aq)} \rightarrow Cu^{2+} + O_{2(aq)} + OH_{(aq)}$	3×10^7	
R6	$Cu^+ + H_2O_{2(aq)} \rightarrow Cu^{2+} + OH_{(aq)} + OH^-$	7×10^3	
R7	$Cu^+ + SO_4^- \rightarrow Cu^{2+} + SO_4^{2-}$	3×10^8	
R8	$Cu^{2+} + HO_{2(aq)} \rightarrow Cu^+ + H^+ + O_{2(aq)}$	$1 \times 10^{8*}$	
R9	$Cu^{2+} + O_2^- \rightarrow Cu^+ + O_{2(aq)}$	$8 \times 10^{9*}$	
R10	$O_2^- + O_{3(aq)} \rightarrow O_{2(aq)} + O_3^-$	$1.5 \times 10^{9*}$	2200^*
R11	$2HO_{2(aq)} \rightarrow H_2O_{2(aq)} + O_{2(aq)}$	8.3×10^5	2720
R12	$HO_{2(aq)} + O_2^- \rightarrow H_2O_{2(aq)} + O_{2(aq)} + OH^-$	9.7×10^7	106
R13	$HO_{2(aq)} + OH_{(aq)} \rightarrow O_{2(aq)}$	1×10^{10}	
R14	$O_2^- + OH_{(aq)} \rightarrow O_{2(aq)} + OH^-$	1.1×10^{10}	2120
R15	$H_2O_{2(aq)} + OH_{(aq)} \rightarrow HO_{2(aq)} + H_2O_{(aq)}$	3×10^7	1680
R16	$HSO_3^- + OH_{(aq)} \rightarrow SO_3^-$	2.7×10^9	
R17	$OH_{(aq)} + SO_3^{2-} \rightarrow OH^- + SO_3^-$	4.6×10^9	
R18	$HSO_3^- + NO_{3(aq)} \rightarrow H^+ + NO_3^- + SO_3^-$	1.3×10^9	2000
R19	$NO_{3(aq)} + SO_3^{2-} \rightarrow NO_3^- + SO_3^-$	3×10^8	
R20	$HSO_4^- + NO_{3(aq)} \rightarrow H^+ + NO_3^- + SO_4^-$	2.6×10^5	
R21	$NO_{3(aq)} + SO_4^{2-} \rightarrow NO_3^- + SO_4^-$	1×10^5	
R22	$NO_2^- + SO_4^- \rightarrow NO_{2(aq)} + SO_4^{2-}$	7.2×10^8	
R23	$O_{3(aq)} + SO_{2(aq)} \rightarrow HSO_4^- + H^+ + O_{2(aq)}$	2.4×10^4	
R24	$HSO_3^- + O_{3(aq)} \rightarrow H^+ + O_{2(aq)} + SO_4^{2-}$	3.7×10^5	5530
R25	$O_{3(aq)} + SO_3^{2-} \rightarrow O_{2(aq)} + SO_4^{2-}$	1.5×10^9	5280
R26	$HSO_4^- + OH_{(aq)} \rightarrow SO_4^-$	3.5×10^5	
R27	$2SO_4^- \rightarrow S_2O_8^{2-}$	6.1×10^8	840
R28	$HSO_3^- + SO_4^- \rightarrow H^+ + SO_3^- + SO_4^{2-}$	5.8×10^8	
R29	$SO_3^{2-} + SO_4^- \rightarrow SO_3^- + SO_4^{2-}$	3.4×10^8	1200
R30	$H_2O_{2(aq)} + SO_4^- \rightarrow HO_{2(aq)} + H^+ + SO_4^{2-}$	1.7×10^7	
R31	$HO_{2(aq)} + SO_4^- \rightarrow H^+ + SO_4^{2-} + O_{2(aq)}$	3.5×10^9	
R32	$O_2^- + SO_4^- \rightarrow O_{2(aq)} + SO_4^{2-}$	3.5×10^9	

No.		k_{298}
R33	$NO_3^- + SO_4^- \rightarrow NO_{3(aq)} + SO_4^{2-}$	5×10^4
R34	$OH^- + SO_4^- \rightarrow OH_{(aq)} + SO_4^{2-}$	1.4×10^7

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

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

No.	Reactions	k_{298}	E_a
E1	$H_2O_{(aq)} \leftrightarrow H^+ + OH^-$	1.8×10^{-16}	
E2	$HO_{2(aq)} \leftrightarrow H^+ + O_2^-$	1.6×10^{-5}	
E3	$Cu^{2+} + OH_{(aq)} \leftrightarrow CuOH^{2+}$	1.17×10^4	
E4	$HO_{3(aq)} \leftrightarrow H^+ + O_3^-$	5×10^{-9}	
E5	$H_2O_{(aq)} + NH_{3(aq)} \leftrightarrow NH_4^+ + OH^-$	1.17×10^{-5}	
E6	$H_2O_{(aq)} + SO_{2(aq)} \leftrightarrow HSO_3^- + H^-$	3.13×10^{-4}	
E7	$H_2O_{2(aq)} \leftrightarrow HO_2^- + H^+$	1.6×10^{-12}	-3700
E8	$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	1.02×10^9	

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

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

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

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

Table 5: Henry's Law constant

No.	Species	H_{298} [M atm^{-1}]	$-\triangle H/R$ [K]

1	O_3	1.14×10^{-2}	-2300
2	O_2	1.3×10^{-3}	-1700
3	HO_2	2×10^3	6600*
4	H_2O_2	7.4×10^4	6615*
5	OH	25	-5280

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

3 Results and Discussion

3.1 Parameter analysis of MARK model

Hygroscopic inorganic particle is one of the most important component of $PM_{2.5}$ in the ambient air. The annual average contribution of inorganic aerosol to $PM_{2.5}$ is between 25% and 48% (Tao et al., 2017), especially NH_4^+, SO_4^{2-}, NO^{3-} and other inorganic ions. In lab studies of radical heterogeneous reactions, $(NH_4)_2SO_4$ aerosol is most widely studied because of its simple components and easy way to generate. Without the interference of organic matter, it is convenient to explore the mechanism of HO_2 heterogeneous uptake and derive its parameterized equation, which provides a good reference for the heterogeneous uptake of HO_2 in the actual atmosphere environment. In this study, $(NH_4)_2SO_4$ aerosol uptake HO_2 is simulated by MARK model, and good correlation between simulation results and experimental results are obtained especially considering the influence of both [Cu] and RH.

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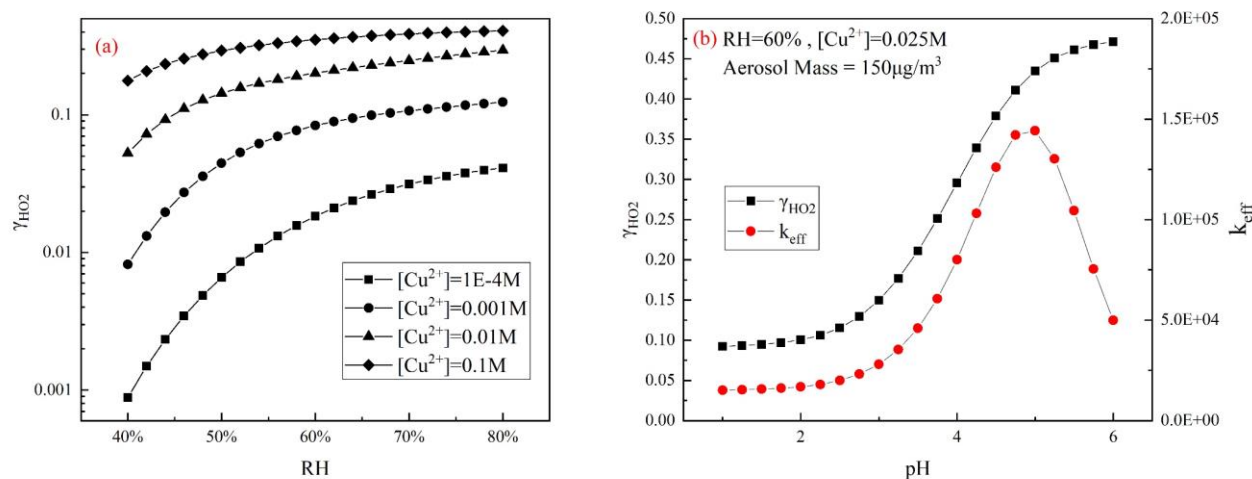
Figure 1: Parameter analysis of the Mark model. (a) γ_{HO_2} increases with the RH at different $[Cu^{2+}]$; (b) γ_{HO_2} in black square dotted line increases with aerosol bulk phase pH and k_{eff} in red circular dotted line has a peak value at about pH=5 then declines quickly.

γ_{HO_2} has an S-shaped growth with aerosol bulk phase pH. k_{eff} is the comprehensive reaction rate constant of HO_2 dissolution equilibrium and liquid phase chemical-physical reaction during HO_2 heterogeneous uptake reaction. In the model, it is found that as the pH rising, the uptake coefficient rises rapidly because HO_2 is a weak acid (pKa = 4.7) and has a low solubility in an acidic environment. The higher bulk phase pH is favorable for the dissolution equilibrium of the gas phase HO_2. On the other hand, aqueous phase reaction rates of HO_2/O_2^- and Cu^{2+} decrease with the increasing of bulk phase pH. The pH of the ambient atmospheric aerosol is generally below 5 even for high NH_3 cases like Beijing and Xi'an(Ding et al., 2019;Guo et al., 2017) with a range of 3~6. At this range, HO_2 heterogeneous reaction is highly affected by aerosol pH indicating the significance of this field of study.

3.2 Model Verification

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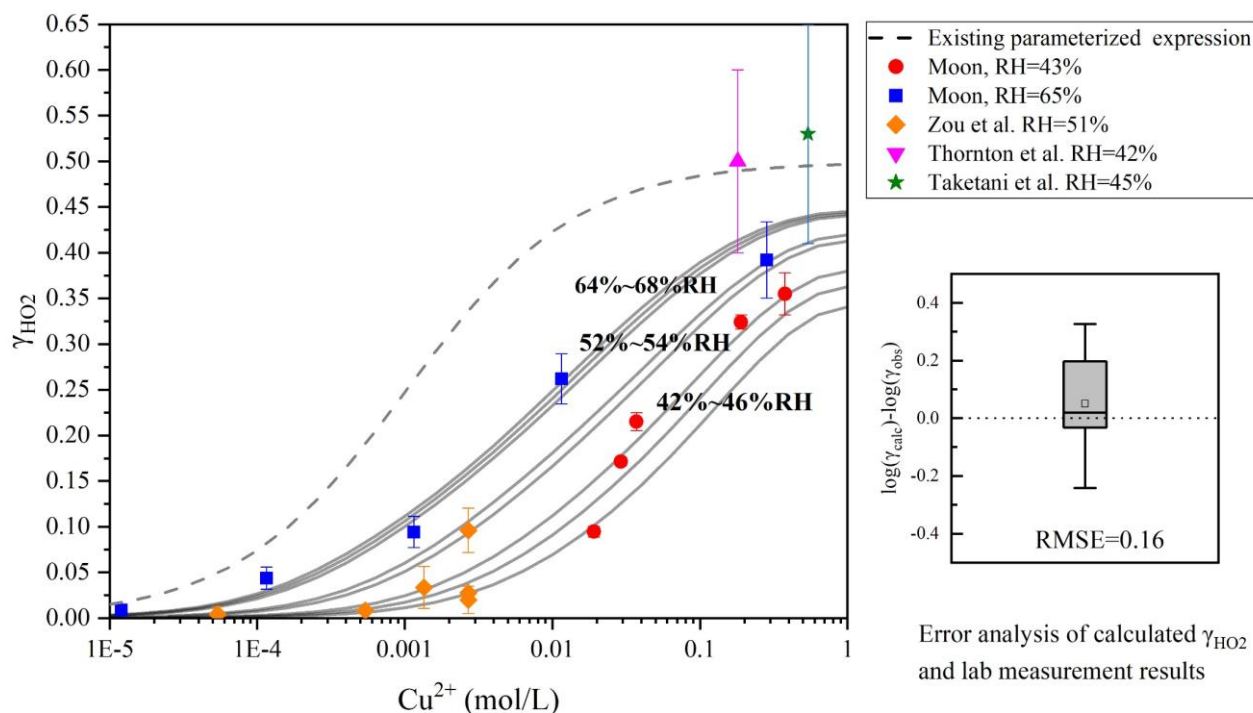
Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red circles denote the results at 43% RH, and blue squares at 65% RH (research by Moon et al., 2018(Moon et al., 2018)). Yellow diamonds denote results at 51% RH (research by Zou et al., 2019(Zou et al., 2019)), inverted triangle at 42%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

As shown in Fig. 2. when the aerosol copper is less than $1\sim2\times10^4$M, the heterogeneous uptake of HO_2 is not significant. As the copper concentration increases, γ_{HO_2} rapidly rises to the limits of accommodation and HO_2 solubility. Many research studies have proposed that ambient RH affects γ_{HO_2} (Thornton and Abbatt, 2005;Thornton et al., 2008;Taketani et al., 2008b, 2009;Taketani and Kanaya, 2010;Taketani et al., 2012;Matthews et al., 2014). For hygroscopic inorganic aerosols, RH significantly affects the aerosol liquid water content, changing its ionic strength, aqueous reagent concentrations, and the effective Henry's coefficient.

In this study, we used MARK model to simulate the observed γ_{HO_2} from all the available lab studies, which were conducted with different ambient RH and Cu^{2+} concentrations(Moon et al., 2018;Zou et al., 2019). In general, good

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200   agreement is achieved between the MARK model results and the results of the previous lab studies, which were also classified based on a statistical parameter: root mean square error (RMSE). The γ_{HO_2} from both the MARK model and lab studies are much smaller than the predicted results from the existing parameterized equations for [Cu^{2+}] (smaller than 0.1 mol L^{-1}). Therefore, a novel parameterized equation is required to better describe the influence of [Cu^{2+}] on γ_{HO_2}.

3.3 A novel parameterized equation for γ_{HO_2}

205   When the full reaction system reaches steady-state, the reaction of HO$_2$ in the aqueous particle phase can be expressed as the following equation(Schwartz, 1984;Schwartz and Meyer, 1986;Schwartz and Freiberg, 1981;Schwartz, 1987)

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

Gas phase HO$_{2(g)}$ molecule transports onto the surface of the aerosol particles HO$_{2(r)}$ then dissolves at the bulk phase HO$_{2(a)}$. Because the reaction between [Cu^{2+}] and HO$_2$ is a catalytic reaction, in the model simulations, the total amount of
210   [Cu^{2+}] concentration in the system does not change with reaction time. The rate of HO$_2$ aqueous reaction with copper ions is noted as k_{eff}. For fine particles, we can safely assume that the interface concentration [HO$_2$] is equal to the bulk phase average $\overline{[HO_2]}$ concentration due to rapid diffusion in the liquid phase(details have been dicussed above). With the definition of the uptake coefficient as $\gamma = \alpha(1 - \frac{c_{a,surf}}{H^{cc}c_{g,surf}})$, we deduce the parameterized equation of γ_{HO_2} in the framework of the resistance model. For the submicrometer Cu(II)-doped particles with which most uptake reaction occurs, the influence of the
215   gas phase diffusion limitation can be neglected.

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

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

where k^{cat} is the pseudo effective catalytic rate, $[Cu^{2+}]_{equ}$ is the equivalent concentration of Cu, And γ_{HO_2} can be
225   expressed as

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{3 \times v}{4 \times R_d \times H_{corr}RTk_{eff}} \tag{14}$$

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

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

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

230

We further calculated the RMSE of the modeled data and parameterized equation data under different RH conditions. All the RMSE values are less than 0.2, which indicates a minor deviation in our γ_{HO_2} equation. Under the typical ambient urban atmospheric environment, aerosol mass concentration of 10~300 μg m^{-3}, aqueous Cu^{2+} concentration of 10^{-5}~1M, relative humidity between 40%~90%, the parameterized equation can be used based on the comparison. For dry conditions where

235 RH% is less than 40%, the equation was not tested due to the lack of lab and model studies. The HO_2 uptake under dry conditions needs further investigation in the future, but probably 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., 2008b;Kanaya et al., 2009;Taketani and Kanaya, 2010;Thornton et al., 2008;Thornton and Abbatt, 2005).

RH(%)	80	76	72	68	64	60	56	52	48	44	40
RMSE	0.056	0.061	0.068	0.078	0.091	0.113	0.118	0.133	0.163	0.191	0.186
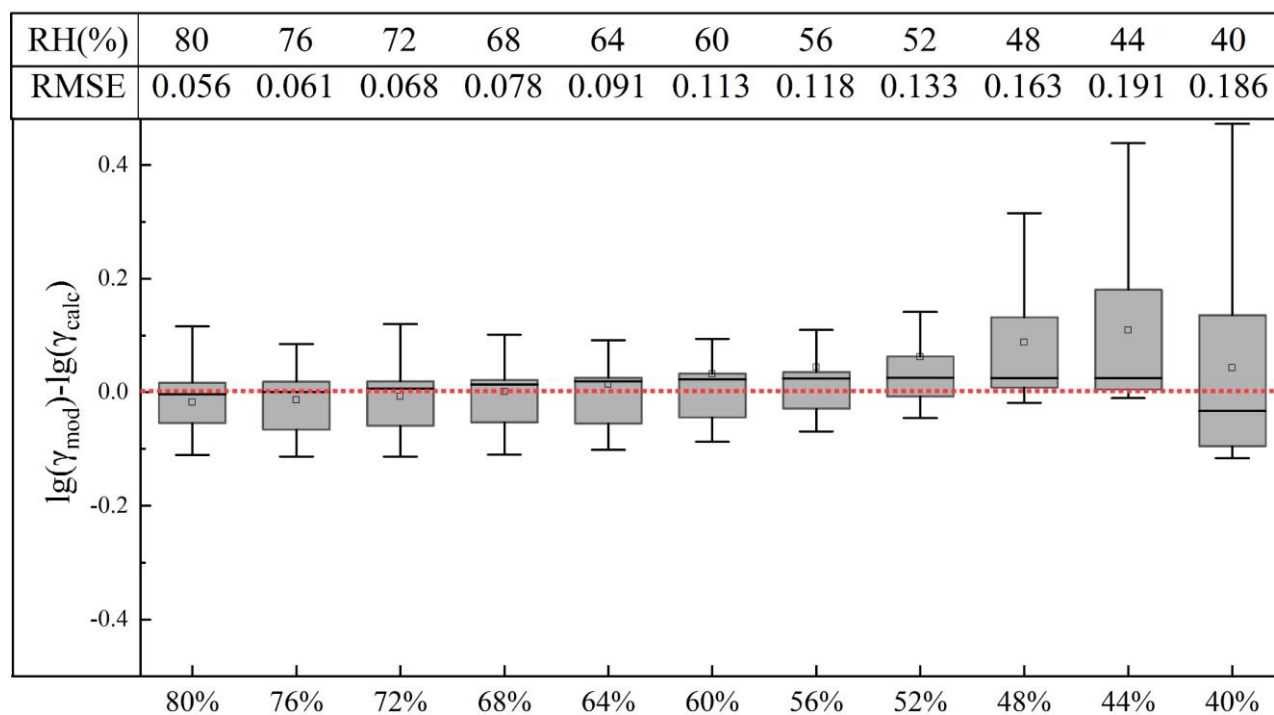
240

Figure 3: Comparison of the modeled γ_{HO_2} and corresponding calculated values from the new parameterized equation. $\log_{10}(\gamma_{mod})$ is the logarithmic value of modeled γ_{HO_2} and $\log_{10}(\gamma_{cal})$ is the calculated value from the new parameterized equation.

3.4 Impact of the HO₂ uptake evaluated with the novel parameterized equation

245   Many model studies(Lakey et al., 2015;Mao et al., 2013b;Martinez et al., 2003;Tie et al., 2001) suggest that heterogeneous uptake of HO_2 radical affects the global distribution of trace gases and the atmosphere oxidant capacity especially in regions with high aerosol loading or low NOx concentration. The importance of aerosol chemistry as a sink for ozone precursors in North China Plain has been suggested in many model studies(Li et al., 2019b;Lou et al., 2014). The competition of HO_2 with aerosol and gas phase reactants is crucial when evaluating the influence of heterogeneous reactions

250   on the atmospheric oxidant capacity.

Based on the results of a comprehensive field campaign performed in summer 2014 in a rural site (Wangdu) in the North China Plain, HO_2 uptake coefficient and the ratios of the HO_2 uptake rates ($TR_{HO2uptake}$) to the sum of the ROx termination rates($TR_{ROxsinks}$) are calculated with direct measurements of the ROx radicals, trace gas compounds and the aerosol properties. The experimental determined ROx termination rates include reaction channels from $OH + NO_2$ / NO, $HO_2 + HO_2$,

255    $HO_2 + RO_2$, $RO_2 + NO$. Considering the solubility and size distribution of aerosol metal copper(Fang et al., 2017;Hsu et al., 2010a;Mao et al., 2013a) we can estimate γ_{HO_2} in daytime and night. Effective soluble Cu^{2+} used in the calculation is 25% of total aerosol metal copper concentration.

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

Wangdu is located in the center of Beijing-Tianjin-Hebei and is a regional site. The observation was carried out in the

260   summer with serious photochemical smog pollutions(Tan et al., 2017). The table summarizes the meteorological and chemical conditions in this field campaign. In terms of parameters such as temperature, pressure and humidity, the Wandu area is a high-temperature and high-humidity stage with a monsoon climate.

Table 6: Average results of observed meteorological parameters and trace gases concentration in Wangdu campaign

Wangdu	Average results
Temperature /°C	27
Pressure /hPa	1000
RH/%	58
O_3/ppb	55.6
NO_x/ppb	10
HONO/ppb	0.8
CO/ppm	0.6
Isoprene/ppb	0.5
HCHO/ppb	7

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

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

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

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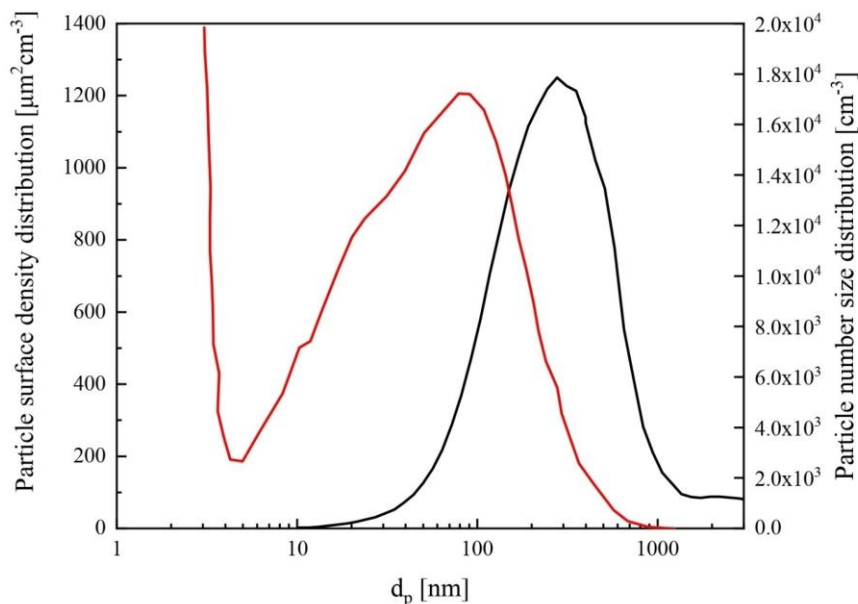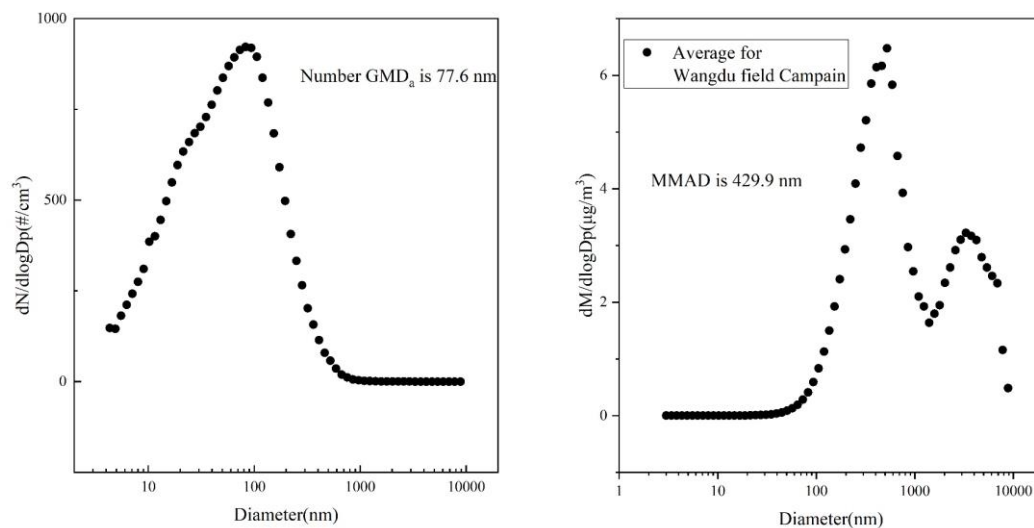

Figure 4: PSSD (black line) and PNSD (red line) of aerosol in Wangdu field campaign

270

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

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

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

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

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

3.4.3 Calculation of soluble copper ion concentration

Since the concentration of soluble copper concentration rather than total copper concentration is used in the model, it is necessary to analyze the ratio of soluble copper to total copper in the aerosol. According to the research results, it is found that the dissolution ratio of copper in aerosol particles from 40% to 60% in different regions(Fang et al., 2017;Hsu et al., 2004;Hsu et al., 2010b).

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

3.4.4 γ_{HO_2} estimated at Wangdu field campaign

By inputting soluble copper concentration, aerosol mass concentration, aerosol particle geometer mean diameter and the corresponding relative humidity and temperature into the empirical equation, we can obtain the estimation of γ_{HO_2} in

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Wangdu suburban, which is shown in Fig.6 (a) and (b). The valid data points are 224 with a time resolution of 1 hour. Average aerosol mass concentration is 67.2 ± 39.7 μg m^{-3}, the average Cu concentration is 35.8 ± 57.7 ng m^{-3}. he GaussAmpfitting shows the median of γ_{HO_2} is 0.109±0.005 in daytime and 0.139±0.007 at night in Wangdu campaign.

305   These values are likely the maximum possible upper limit of γ_{HO_2} for near-ground layer aerosols. Because of the distribution of TMI is mainly in the accumulation and coarse mode of aerosol, with the height increasing, the amount of copper in the aerosol decreases, leading to a decrease in the heterogeneous reaction rate of HO$_2$. The current empirical equation can only predict the maximum γ possible value of HO$_2$ heterogeneous uptake. When the aerosol mass concentration is constant, the gas phase resistance increases with the increasing of particle size, then the heterogeneous uptake coefficient

310 of HO$_2$ is further reduced with larger particles. At the same time, the empirical equation can only estimate γ_{HO_2} at relative humidity of 40% to 90%, γ_{HO_2} is lower at the surface of dry aerosol. This further led to an overestimation of the HO$_2$ heterogeneous uptake coefficient in this campaign. The interaction between organics and soluble copper and the influence of organics on aerosol properties will lead to further uncertainty of uptake coefficient. Lakey et al.(Lakey et al., 2016a;Lakey et al., 2015;Lakey et al., 2016b) have also shown that the addition of a organic compound to Cu(II) doped aerosols, such as

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

         Taketaniet al. collected the filter samples of aerosol in Mts. Tai&Mang, North China(Taketani et al., 2012) and re-aerosolize from the water extracts of sampled particles. The measured uptake coefficients for Mt. Tai samples ranged between 0.09 and 0.40, while those at Mt. Mang were between 0.13 and 0.34. Because of the re-aerosol dissolution of

320 particle filters by acid digestion, soluble copper and other TMI may higher than ambient aerosol particles, which may be the reason of overestimation of the HO$_2$ uptake coefficient. Li et. al(Li et al., 2019b) find that the rapid decrease of PM$_{2.5}$ in China will slow down the reactive uptake rate of HO$_2$ radicals by aerosol particles may be a very important and pervasive factor for the increase in ozone in the North China Plain. They take γ_{HO_2} as 0.2 in their model calculation. However, the results of the MARK model and empirical equation calculations in this paper suggest that HO$_2$ uptake coefficient is in

325 general smaller and highly variable. Thus further research is needed to study the effects of heterogeneous uptake of HO$_2$ on gas phase and heterogeneous physicochemical reactions under different environmental conditions in different regions and when the variability of γ_{HO_2} is considered..
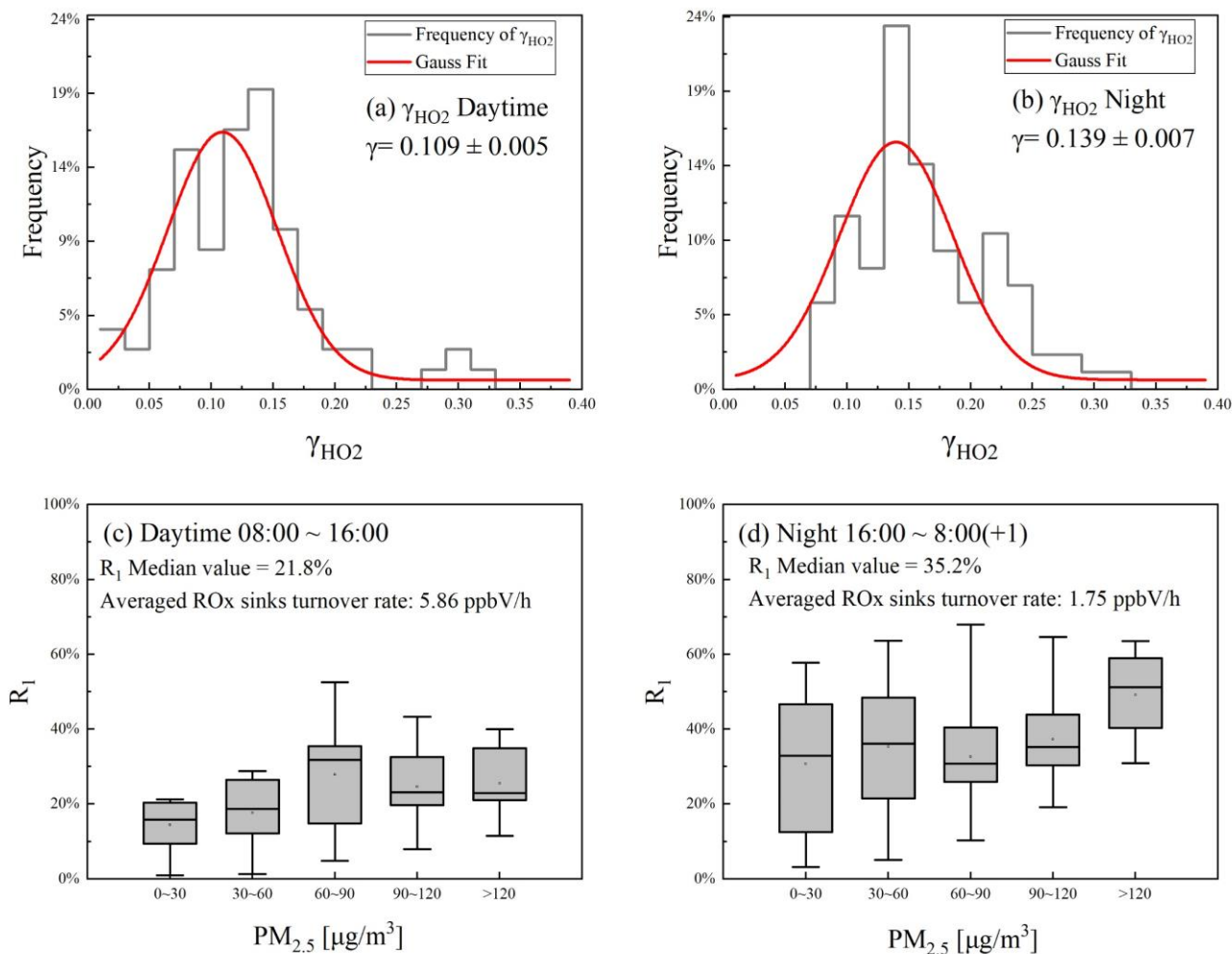
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Figure 6: Daytime and night γ_{HO_2} and R_1 calculated based on the new empirical equation. A Gaussian distribution (red line)
is fitted to γ_{HO_2} frequency distribution in panel (a) and (b), yielding a mean uptake coefficient of 0.109 with a standard error
of 0.005 in daytime and 0.139 with 0.007 at night. Box plot of R_1 according to aerosol mass concentration are shown in
panel (c) and (d). No significant difference of R_1 in the whole range of aerosol mass loading may indicating that HO_2 uptake
is equally important at different aerosol concentration. Daytime ratio is higher than it at night because of the low
concentration of radicals hence the declines of ROx radical self reactions.

The experimental determined ROx termination rates include reaction channels from $OH + NO_2 / NO$, $HO_2 + HO_2$, $HO_2 + RO_2$, $RO_2 + NO$. Considering the solubility and size distribution of aerosol metal copper(Fang et al., 2017;Hsu et al., 2010a;Mao et al., 2013a) we can estimate γ_{HO_2} in daytime and night. Effective soluble Cu^{2+} used in the calculation is 25% of total aerosol metal copper concentration.

340
$$TR_{HO2uptake} = k_{uptake} \times [HO_2] \tag{20}$$

$$R_1 = \frac{TR_{HO2uptake}}{TR_{HOxsinks}} \tag{21}$$

In Fig. (6), no significant difference of γ_{HO_2} is observed during daytime and night. This shows that uptake process may be even more important on ROx budget with low radical concentration at night despite higher NOx concentration. The median values of R_1 in daytime and night have a small rise at relatively high aerosol concentration while having great uncertainties.

345 Averaged daytime (08:00~16:00) ROx radical sinks turnover rate is 5.9 ppbV/h and that for nighttime (16:00~08:00(+1d)) is 1.7 ppbV/h.

3.4.5 The Uncertainty of the calculation in Wangdu campaign

Uncertainty of the calculation in this paper mainly come from the measurement of copper concentration, radical concentration and aerosol liquid water content. The combined standrad uncertainty (u_r) of the model calculations is a

350 combination of uncertainties in the measurements used as model constraints and reaction rate constants. What's more, a series of tests based on Monte Carlo simulations show that the uncertainty of the model calculations is approximately 40%(for details, see Lu et al., 2012 and Tan et al., 2017)(Lu et al., 2012;Tan et al., 2017).

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

Measurement quantities	1σ Accuracy
Cu	±1.3%
Particle number size distribution (PNSD)	±2%
Relative humidity	±0.05%
Temperature	±0.05%
ALWC	±9.1 %
HO$_2$	±16%
RO$_2$	±18%
OH	±11%
NO	±20%
NO$_2$	±20%

355

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

360

$$N = F(x, y, z, \dots) \tag{21}$$

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

Where N is the indirect measurement quantity. u_{r_meas} is the relative combined standard uncertainty of the indirect

365   measurements used as model constraints. x, y, z and other direct measurement quantities are independent physical quantities

refer to RH, copper concentration... The corresponding relative combined uncertainties are u_x, u_y, u_z... They inevitably affect

the indirect measurement, so that the N value also has a corresponding uncertainty u. Since the uncertainty is a small amount,

which is equivalent to the "increment" in mathematics, the calculation formula of the uncertainty of indirect measurement is

basically the same as the total differential equation in mathematics.

370   **4 Summary and conclusions**

The impact of HO_2 uptake on ROx budget is complicated with great uncertainties at the ambient conditions (the combined

standard uncertainty of γ_{HO_2} is ±40.7%, of $TR_{HO2uptake}$ is ±43.7%, of R_1 is ±59.4%.). A fixed value of γ_{HO_2} used in models

may cause errors when evaluating the atmospheric oxidant capacity. The new parameterized equation in this paper provides

a novel way for more detailed calculation of the effects of HO_2 heterogeneous reactions on atmospheric radical budget,

375   ozone production and particulate matter generation. In addition, many model calculations suggest that other soluble TMIs,

including Fe(II)/Fe(III) and Mn(II)/Mn(III), play a similar role in cloud droplets(Graedel and Weschler, 1981;Graedel et al.,

1986). The Cu-Fe and Fe-Mn redox coupling mechanism in clouds requires further research. In ambient aerosol, Fe

concentration is about 10~100 times(Mao et al., 2013a) higher than that of Cu, and for an aerosol pH ranging from 3~6, the

solubility of Fe (primarily Fe^{2+}) is rather small(Fang et al., 2017;Hsu et al., 2010a;Baker and Jickells, 2006;Oakes et al.,

380   2012). The reaction rates of Fe/Mn for liquid phase HO_2 in aerosol is about 100 times slower than it is for Cu. The influence

of aerosol Fe and Mn on HO_2 uptake can be neglected compared to Cu or scaled as equivalent $[Cu^{2+}]$ according to the

difference of their rate constants with HO_2. Overall, we can conclude that the HO_2 uptake process needs to be considered in

the photochemical box model for the study of the HOx radical budget. The exact value is highly variable with respect to the

change of copper concentrations in the aerosol liquid water. The measurement of soluble copper and other TMIs as well as

385   the aerosol liquid water shall be added for future field campaign for the study of HOx radical budget.

Author contribution

Keding Lu and Yuanhang Zhang conceived the study. Xiaorui Chen and Qi Zou modified the codes. Keding Lu, Zhaofeng

Tan and Hendrik Fuchs revised the manuscript critically. Andreas Wahner and Astrid Kiendler-Scharr provided the data of

radical concentrations in Wangdu campaign. Alfred Wiedensohler and Mei Zheng provided the data of aerosol compositions.
390 Huan Song performed the model simulations and prepared the manuscript which was enhanced by contributions from the co-authors.

Competing Interest

The authors have no conflict of interests.

Data avaiability

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

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