Influence of aerosol copper on HO_2 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 Wiedensohler[4], Daniel R. Moon[5,6], Dwayne E. Heard[5], Maria-Teresa Baeza-Romero[7], Mei Zheng[1], Andreas Wahner[2,3], Astrid Kiendler-Scharr[2,3], Yuanhang Zhang[1,2]

1. State Key Joint Laboratory or 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 Ingeniería Industrial y Aeroespacial de Toledo, , 45071, Toledo, Spain

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

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

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

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

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 hydroperoxyl (HO_2) radical. In the established chemical mechanism, the coupling of OH and HO_2 is strongly determined by the reaction of OH + VOCs (volatile organic compounds)/CO/HCHO/CH_4/H_2/SO_2 and HO_2 + NO (Seinfeld, 1986). The reactivity from aerosol uptake cannot compete with the known gas phase reactivity of OH, whereas it may compete with the reactivity of NO toward HO_2 under some conditions such as low NO (Tang et al., 2017). For high aerosol mass load, the reaction rate of HO_2 with aerosol particles could be fast enough to influence the concentration of HOx radicals, and consequently, reduce ozone production from HO_2+NO (Kanaya et al., 2009;Li et al., 2019b).

From a global perspective, the impact of HO_2 uptake on the calculated HOx concentrations is diagnosed to be about 10∼40 % (Jacob, 2000;Whalley et al., 2015;Whalley et al., 2010;Mao et al., 2010;Li et al., 2019b;Li et al., 2019a) and often the value of γ_{HO2} (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 impact of HO_2 uptake 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), 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-dopped ammonium sulphate aerosols at 43% relative humidity and proposed a novel parameterized equation for the prediction of γ_{HO_2} that best fits all the laboratory results. Furthermore, 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 (=OH + HO_2) budget was evaluated.

2 Materials and Methods

2.1 The Model

A Multiphase Reaction Kinetic Model (MARK) is developed in this study for the simulation of γ_{HO_2} for the laboratory experiments. The reaction mechanism and reaction rate constants are summarized in Table S.1 – S.4in the Supplementary Information (SI). The MARK model is currently capable of simulating inorganic deliquescent aerosol at ambient pressure and temperature. The model directly calculates the quasi-first order gas phase uptake loss rate, k_{het}(s^{-1}), in Eq. (1). In this model, aerosol liquid water content (ALWC) [g cm^{-3}] is more pertinent than surface density because of the influence of the *RH* on the uptake process (Kuang et al., 2018;Bian et al., 2014).

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

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

where R_d is Count Median Radius of aerosols[cm] , v_{HO_2} is the mean molecular speed of HO_2 [cm s^{-1}] and D_g is the gas phase diffusion coefficient [cm^{2}s^{-1}], ρ is the density of the aerosol particles [g cm^{-3}]. The units of aqueous reagents are converted to [molecule cm^{-3}] in the model by k_{mt}.

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

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

k_{mt} is used to connect the gas phase reactions and the aerosol condensed phase reactions. The rate of gas phase reactants (X) diffusing and dissolving to the condensed phase can be calculated in the framework of aqueous phase reactions as $k_{mt\_X} \times ALWC$ (where X is the reactant molecule). Moreover, the conversion rate of aqueous phase reactants to gas phase can be calculated as $\frac{k_{mt\_X}}{H^{cc} \times RT}$ where H^{cc} is the effective Henry's law constant [M atm^{-1}]. The unit of k_{mt} is s^{-1}, as k_{mt} contains the conversion from m_{air}^{-3} of the gas phase molecule concentrations to m_{aq}^{-3} of the aqueous phase molecule concentrations and in the other direction. For larger particles (radius >1 µm), k_{mt} is mainly determined by gas phase diffusion of HO_2. For smaller particles (radius <1 µm) k_{mt} is mainly determined by the accommodation coefficient (α). The MARK model can simultaneously simulate gas and liquid two-phase reaction systems in the same framework.

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

2.2 Corrections to γ_{HO_2} in the MARK model

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^{cc} is the effective Henry's law constant [M atm^{-1}], H_0 is the physical Henry's law constant, 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}:

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

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

$$A_{HO_2} = 10^{-0.1\times I} \quad (5)$$

According to this correction, H^{cc} of HO_2 increases with RH and decreases quickly after [Cu^{2+}] reaches 0.1M in aerosol liquid phase, which limits γ_{HO_2} 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.

In ambient aerosol, though the Fe concentration is about 10−100 times (Mao et al., 2013a) higher than that of Cu, for an aerosol pH ranging from 3−6, the solubility of Fe (primarily Fe^{2+}) is rather small (Fang et al., 2017;Hsu et al., 2010a;Baker and Jickells, 2006;Oakes et al., 2012). The reaction rates of Fe/Mn for liquid phase HO_2 in aerosol is about 100 times slower than it is for Cu. For these reasons, the influence of aerosol Fe and Mn on HO_2 uptake can be neglected compared to Cu or scaled as equivalent [Cu^{2+}]. Thus, in this paper, we only focused the crucial influence of aerosol coppper on HO_2 uptake.

At low relative humidity, the aqueous phase is highly concentrated (i.e. with a high ionic strength), and the solution is strongly non-ideal, 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.

Based on Ross and Noone (Ross and Noone, 1991), for an ion (X_i) of charge z_i, the activity coefficient (φ_x) is

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

where D is given by equation (7):

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

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

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

$\varepsilon(x,y,I)$ 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, 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 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 ($[x_i]_{equ}$) can be calculated as:

$$[x_i]_{equ} = [x_i] \times \varphi_x \quad (10)$$

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 HO_2. The effective concentration of Cu ion can be calculated as:

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

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

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

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

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

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^{2}s^{-1}], k_{eff} is the comprehensive reaction rate coefficient which encompasses both HO_2 dissolution equilibrium reactions and liquid phase chemical-physical reactions during HO_2 uptake process. In the copper-doped aerosol particle, because of the high value of k_{eff} and small Count Median Diameter (R_d) (usually smaller than 1 μm), the ratio is close to 1. At a diameter of 1 μm, and a relative humidity between 40% and 90%, the condensed phase copper ion concentration varies from 10^{-5} to 1M, the average ratio of the surface HO_2 concentration and the condensed phase HO_2 concentration is 0.89. At 400nm diameter particles for RH = 40% to 90%, the ratio is larger than 0.95. The ratios are calculated by simulation of k_{eff} and the accordingly calculations by Equation (12) and (13). Thus, in this model, we assume the surface concentration of HO_2 equals to the condensed phase average HO_2 concentration.

2.3 Laboratory results for the HO_2 accommodation coefficient

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

The accommodation coefficient of HO_2 used in the model was determined for copper-doped inorganic aerosol particles using values taken from various previous laboratory studies. The 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).

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 the accommodation coefficient α_{HO_2} as 0.5.

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})	α_{HO_2}	Ref.
NH_4HSO_4	75%	0.0059−0.067*	0.40±0.21	(Mozurkewich et al., 1987)
$(NH_4)_2SO_4$	45%	0.5	0.53±0.13	(Taketani et al., 2008)
$(NH_4)_2SO_4$	42%	0.16	0.5±0.1	(Thornton and Abbatt, 2005)
$(NH_4)_2SO_4$	53−65%	0.5−0.7*	0.4±0.3	(George et al., 2013)
$(NH_4)_2SO_4$	65%	0.57	0.26±0.02	(Lakey et al., 2016b)
$(NH_4)_2SO_4$	51%	0.0027	0.096±0.024	(Zou et al., 2019)
$(NH_4)_2SO_4$	43%	0.38	0.355±0.023	This work
NaCl	53%	~0.5	0.65±0.17	(Taketani et al., 2008)

KCl	75%	5% of KCl solution	0.55±0.19	(Taketani et al., 2009)
$LiNO_3$	75%	0.03−0.0063*	0.94±0.5	(Mozurkewich et al., 1987)

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

3 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 in order to derive a parameterized equation for the uptake coefficient, γ_{HO_2}, and which did not consider any potential role of organic matter present in the aerosol because of the reasons detailed below.

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

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

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

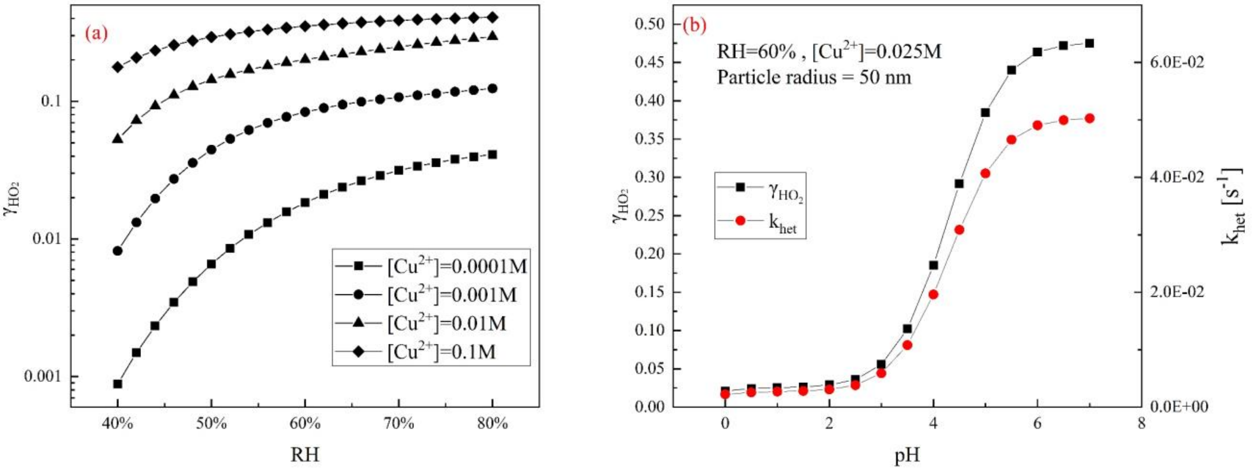

Figure 1: Influence of various parameters upon γ_{HO_2} predicted by the MARK model. (a) γ_{HO_2} increases with the *RH* at different [Cu^{2+}]; (b) γ_{HO_2} denoted by black squares and black line and k_{het} in red circles and red line increase with aerosol particle condensed phase pH.

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 may mainly because of the change of solubility.

3.2 Model Validation

In this study, we used the MARK model to simulate the observed γ_{HO_2} from all the available laboratory studies, which were conducted with different ambient *RH* and Cu^{2+} concentrations (Zou et al., 2019;Lakey et al., 2016b;Thornton and Abbatt, 2005;Taketani et al., 2008). In general, good agreement is achieved between the MARK model results and the results of the previous laboratory studies, which were also classified based on a statistical parameter: root mean square error (RMSE) (Figure 2).

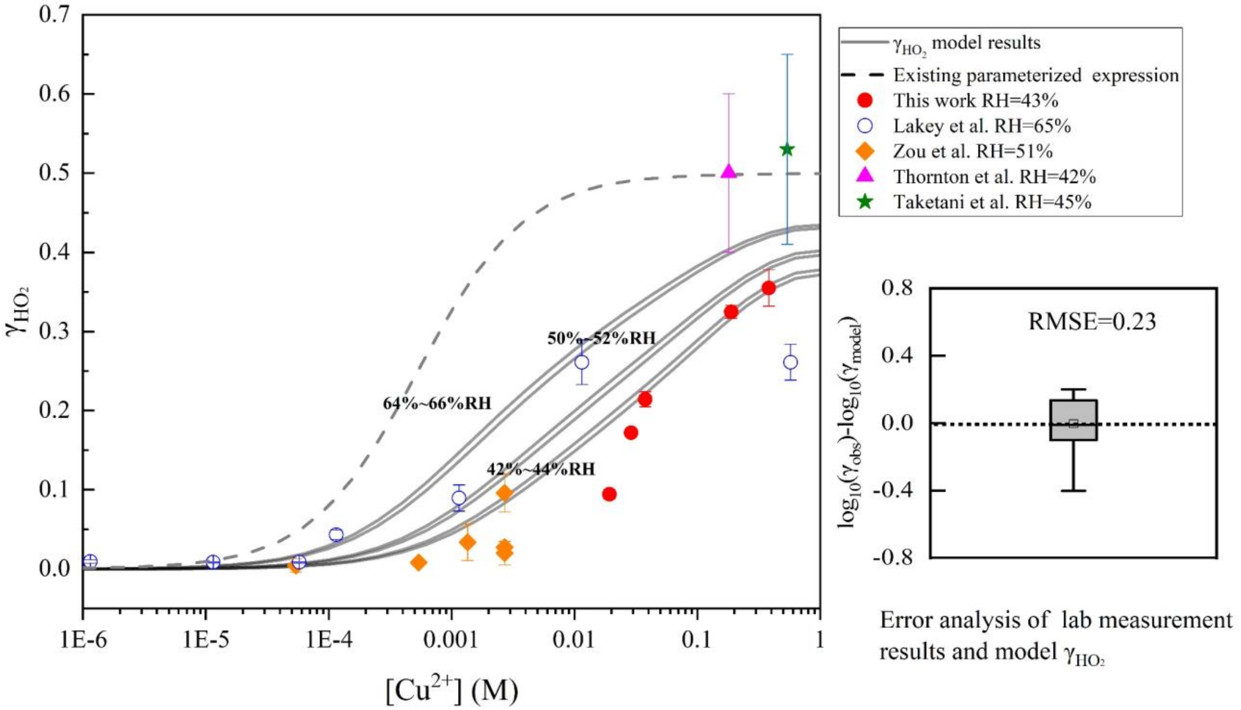

Figure 2: Dependence of γ_{HO_2} on aerosol copper concentration. Red filled circles denote the results at 43% *RH* measured at Leeds. Blue hollow circles at 65% *RH* (Lakey et al., 2016b). Yellow filled diamonds denote results at 51% *RH* (Zou et al., 2019), filled purple triangle at 42% *RH* (Thornton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

As shown in Fig. 2. when the condensed phase copper ion concentration is less than $1\text{-}2\times10^{-4}$ M, the heterogeneous uptake of HO_2 is not significant. This threshold is consistent with the results of previos researches (Mozurkewich et al., 1987;Lakey et al., 2016b). As the copper concentration increases, γ_{HO_2} rapidly rises to the limit of the accommodation coefficient determined by the HO_2 solubility. Many research studies have proposed that ambient *RH* affects γ_{HO_2} (Thornton et al., 2008;Taketani et al., 2008, 2009;Taketani and Kanaya, 2010;Taketani et al., 2012;Matthews et al., 2014;Thornton and Abbatt, 2005). For hygroscopic inorganic aerosols, *RH* significantly affects the aerosol liquid water content, changing its ionic strength, aqueous reagent concentrations, and the effective Henry’s coefficient.

The deviation of γ_{HO_2} between the MARK model and laboratory studies is smaller than the predicted results from the existing parameterized equation (Thornton et al., 2008;Hanson et al., 1992;Hanson et al., 1994;Jacob, 2000;Kolb et al., 1995;Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.) as shown in Figure 2. In order to reduce the overestimation of the existing parameterized equation, we used the effective rate constant of HO_2 (O_2^-) with Cu ions as 1.5×10^7 M^{-1} s^{-1} rather than the more commonly used value of 1×10^9 M^{-1} s^{-1} according to the research by Bielski in 1985 (Bielski et al., 1985) considering the pH limitation (pH is about 3-5 in ambient aerosol particle condensed phase as dicussed above). The prior value (1.5×10^7 M^{-1} s^{-1}) reflects the rate of reaction between HO_2 and Cu^{2+}, more prevalent in acidic aerosol such as ammonium sulphate, and the latter between O_2^- and Cu^{2+} ions, which is more prevalent in aerosols with a pH greater than the pK_a of HO_2, such as NaCl (Bielski et al., 1985). This treatment within the calculation can bring predictions more in line with experimental results compared to the high value of 1×10^9 L $mol^{-1}s^{-1}$ used in the existing parameterized equation. IUPAC (Ammann et al., 2013;IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.) proposed the effective rate coefficient for the reaction of HO_2 (O_2^-) with Cu ions as $5x10^5$ M^{-1} s^{-1} to achieve the best fit based on the calculation results from Lakey et al. (2016b). This assumption is not in accordance with the aqueous reaction rate coefficient from other databases mentioned below, and needs further laboratory measurements to confirm it. According to the aqueous reaction rate coefficient from NIST and the latest measurement result (Lundström et al., 2004;Huie, 2003), the rate coefficient of HO_2 with Cu^{2+} is 1×10^8 or 1.2×10^9 M^{-1} s^{-1} at pH= 2 and pH=1, respectively. These two rate coefficients were quantified in a low pH environment (pH=2 for 1.2×10^9 M^{-1} s^{-1} and pH=1 for 1×10^8 M^{-1} s^{-1}). At the same time, the reaction rate of O_2^- with Cu^{2+} is 8×10^9 M^{-1} s^{-1} for pH in the range 3-6.5 (Huie, 2003). At higher pH, the reaction rate of HO_2 with Cu^{2+} may change, but it is unknown whether it will decrease by four orders of magnitude. Further kinetics experiments are needed at varying pH to verify the reaction rate coefficient of Cu^{2+} ions with HO_2 and O_2^- in aqueous solution. The rate constants used in the MARK model are shown in the Table S. 1 in the SI. The main reason for the differences between the original parameterization and the MARK model is the effect of including the activity coefficients of Cu ions and HO_2 and the effects of reactions of different valence states of copper ions. Considering the small RMSE between the MARK model and the laboratory studies, we proposed a novel parameterized equation to better describe the influence of $[Cu^{2+}]$ on γ_{HO_2}.

3.3 A novel parameterized equation of γ_{HO_2}

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

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

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 $Cu^{2+}/Cu^{+}$and HO_2 can be seen as catalytic reactions, because in the model simulations, the total amount of $[Cu^{2+}]+[Cu^{+}]$ does not change with reaction time. For fine particles, we can safely assume that the interface concentration $[HO_{2(\mathrm{r})}]$ is equal to the condensed phase average $\overline{[HO_2]}$ concentration due to rapid diffusion in the liquid phase (details have been dicussed in section 2.2.3). For the submicrometer aerosol particles with which most uptake reaction occurs, the influence of the gas phase diffusion limitation can be neglected. Hanson et al. (1994) proposed the definition of the uptake coefficient as $\gamma = \alpha(1 - \frac{c_{a,surf}}{H^{cc}c_{g,surf}})$ where $c_{a,surf}$ is the suface concentration of the reactant, $c_{g,surf}$ is the gas phase concentration. In the process of HO_2 uptake, we deduce the parameterized equation of γ_{HO_2} in the framework of the resistance model:

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

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

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

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

From Eq. (15), it can be deduced that γ_{HO_2} can be calculated by optimizing k_{eff} under different ambient environmental conditions. The MIPFIT model (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 condensed phase soluble copper concentration $[Cu^{2+}]$ with an exponential relationship to the parameterization of the catalytic reactions, which is denoted in Eq. (16). The exponent of $[Cu^{2+}]$ is globally fitted using the MIPFIT method. It is found that the overall R^2 is higher than 0.97 and the residual is minimized when the exponent is 0.65. $f(\mathrm{ALWC, [PM]})$ has a negative exponential relationship to [PM], and has a positive linear relationship to *RH*.

We further calculated the RMSE of the modeled data and parameterized equation (15) data under different *RH* conditions. The range of values shows the difference between the modeled data and parameterized equation data at different Cu^{2+} concentration. At low *RH* and consequently relatively low ALWC, γ_{HO_2} is more sensitive to $[Cu^{2+}]$ expecially at low $[Cu^{2+}]$ ($<10^{-4}$M). This sensitivity can not be fully represented in the parameterized equation. What is more, at low $[Cu^{2+}]$ and low *RH*, the value of γ_{HO_2} is smaller than in other conditions, so that the uncertainty of γ_{HO_2} becomes larger.

All the RMSE values are 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 μg m^{-3}, aqueous Cu^{2+} concentration of 10^{-5}-1M, and a relative humidity between 40%-90%, the parameterized equation can be used. The HO_2 uptake under dry conditions needs further investigation in the future, but probably is not of high priority because the effective reaction volume becomes 10% or less of the aerosol volume for dry conditions and the HO_2 uptake may then be neglected for typical tropospheric conditions (Taketani et al., 2008;Kanaya et al., 2009;Taketani and Kanaya, 2010;Thornton et al., 2008;George et al., 2013).

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

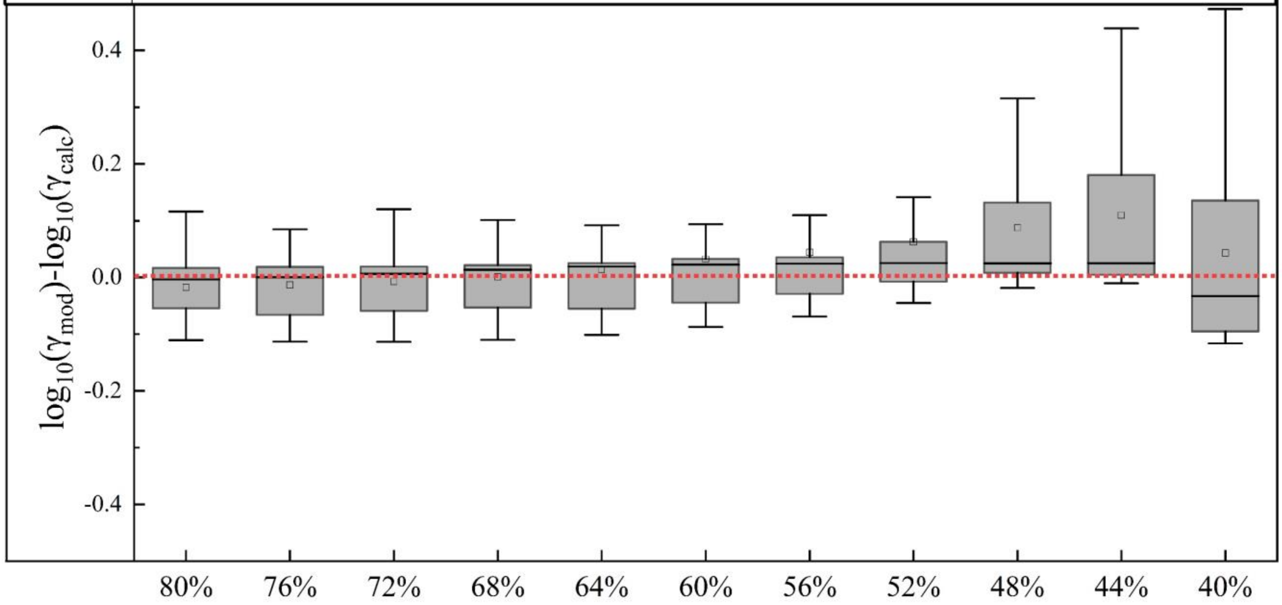

Figure 3: Comparison of the MARK modeled γ_{HO_2} to the corresponding calculated values from the new parameterized equation (15). $log_{10}(\gamma_{mod})$ is the logarithmic value of modeled γ_{HO_2} and $log_{10}(\gamma_{cal})$ is the calculated value from the new parameterized equation (15).

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

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

Based on the results of a comprehensive field campaign performed in summer 2014 in a rural site (Wangdu) in the North China Plain(Tan et al., 2020), the HO_2 uptake coefficient and the ratios of the HO_2 uptake loss rates ($TR_{HO2uptake}$) to the sum of the ROx termination rates ($TR_{ROxsinks}$) are calculated with direct measurements of the ROx radicals, trace gas species, ALWC and the aerosol condensed phase component concentrations (please see the SI for details). The experimental determined ROx termination rates include reaction channels from OH + NO_2, OH + NO, HO_2 + HO_2, HO_2 + RO_2 and RO_2 + NO. Considering the solubility and size distribution of particle metal copper (Fang et al., 2017;Hsu et al., 2010a;Mao et al., 2013a) we can estimate γ_{HO_2} in daytime and night.

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

Wangdu is located in the center of the Beijing-Tianjin-Hebei area and is a regional site. The observation was carried out in 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 humidity, the Wangdu area is a high-temperature and high-humidity environment with a monsoon climate.

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	1σ Accuracy
Temperature /℃	27±4	±0.05%
Pressure /hPa	1000±5	±0.05%
RH/%	61±18	±0.05%
O_3/ppb	55.6±9.0	±5%
NO_x/ppb	10±13.6	±20%
HONO/ppb	0.8±0.24	±20%
CO/ppm	0.6±0.19	<5%
Isoprene/ppb	0.5±0.11	±15%-20%
HCHO/ppb	7±0.69	±5%

3.4.2 Calculation of soluble copper ion concentration

For particle radius smaller than 2.5μm, which are the most contributing bins of aerosols in HO_2 uptake, the mass fraction of Cu is about 33%−100% in four size bins in ambient aerosols (<1μm, 1-2.5 μm, 2.5-10 μm, >10μm) (Mao et al., 2013a). During this campaign, the total concentration of heavy metal ions in fine particles (smaller than 2.5μm) was measured using a commercial instrument based on non-destructive X-ray fluorescence technique (Xact 625, Cooper Environmental). Since the concentration of soluble copper concentration rather than total copper concentration is used in the model, it is necessary to analyze the ratio of soluble copper to total copper in the aerosol particles. According to previous research results, the dissolution ratio of copper in aerosol particles varies from 20% to 70% in different regions, being solubility lower in smaller particles (Fang et al., 2017;Hsu et al., 2004;Hsu et al., 2010b). Therefore, when using the empirical paraterization equation (Eq.15) to calculate the HO_2 heterogeneous uptake coefficient, it is necessary to reduce the copper concentration considering the solubility and the distribution in the accumulation mode of aerosol particles. We take 50% copper is soluble in the particle condensed phase and 50% copper is in the accumulation mode. Thus we assume 25% of total aerosol metal copper concentration is soluble in the accumulation mode when calculating γ_{HO_2} in Wangdu campaign. The aerosol liquid water content is divided by the hourly resolution total copper concentration (ng m^{-3}) and the atomic mass of copper (64) to obtain the total copper molarity in the aerosol (mol L^{-1}).

3.4.3 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 empirical equation, 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). Average aerosol mass concentration is 67.2±39.7 μg m^{-3}, the average Cu concentration is 35.8±57.7 ng m^{-3}. The results of a fit to a GaussianAmp function results in a γ_{HO_2} median value of 0.109 ± 0.045 in daytime and 0.130±0.053 at night in the Wangdu campaign (γ_{HO_2} will increase 1.57 times from 0.075±0.031 at 10% solubility to 0.193±0.079 at 70% solubility for the summary of day and night data).

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

The experimentally determined ROx termination rates include reaction channels from OH + NO_2, OH + NO, HO_2 + HO_2, HO_2 + RO_2, RO_2 + NO. The ratio (R_1) of HO_2 uptake loss rate ($L_{HO2uptake}$) to the whole RO_x loss rate (L_{ROx}) is calculated by Equation (20) and (21).

$$L_{HO2\text{uptake}} = 0.25 \cdot v_{HO_2} \cdot [ASA] \cdot [HO_2] \tag{20}$$

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

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

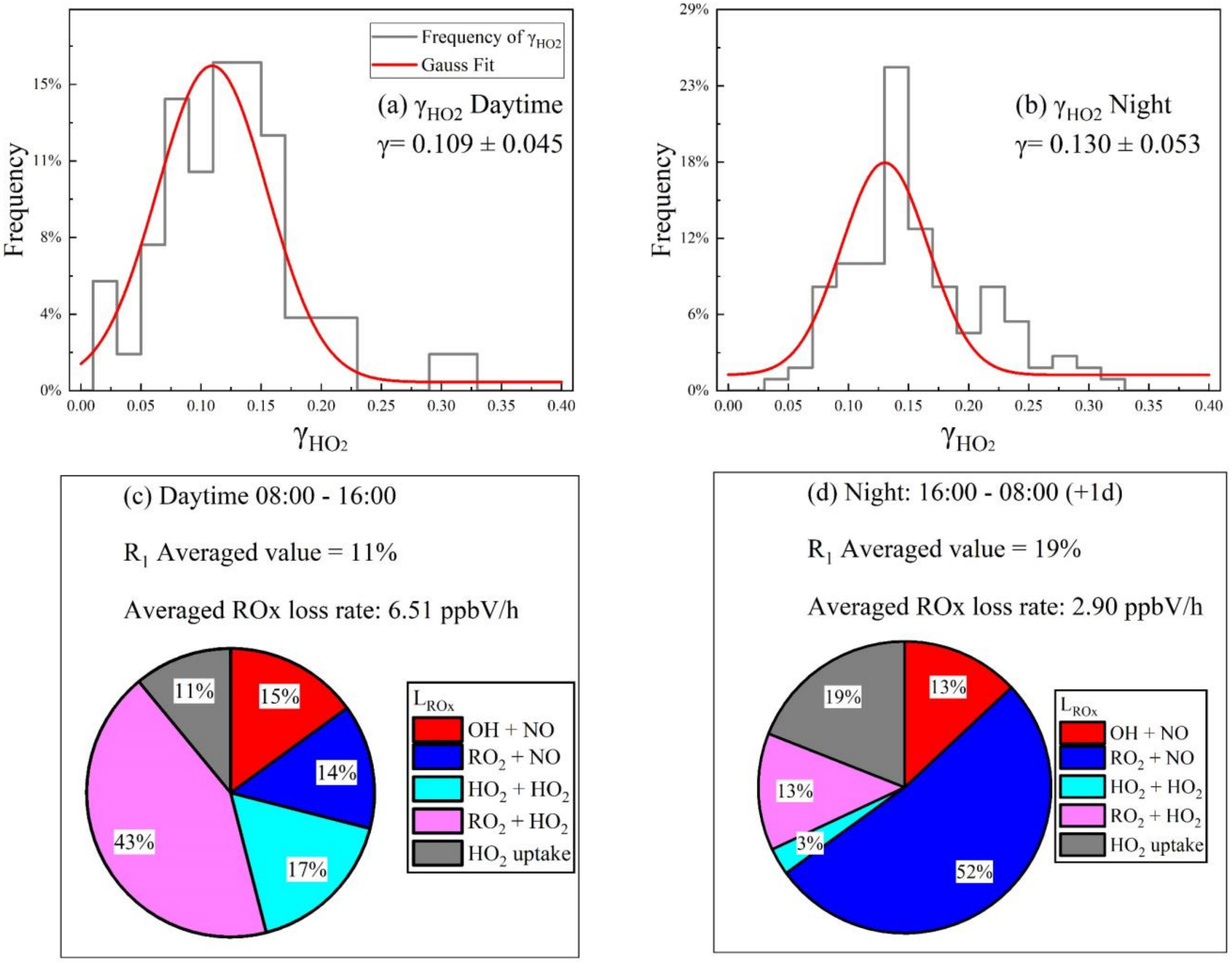

Figure 4: Daytime and night values of the HO_2 uptake coefficient (γ_{HO_2}) and R_1 calculated by the empirical equation (Equation 15). A Gaussian distribution (red line) is fitted to frequency distribution of γ_{HO_2} (a) and (b) yielding a mean uptake coefficient of 0.109 with a standard error of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

In Fig. (4 a and b), no significiant 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). HO_2 heterogeneous uptake reactions with aerosol particles have small impact on ROx radical termination at daytime as shown in Fig. (4 c). However, HO_2 uptake may be important in the termination of ROx radicals at night shown in Fig. (4 d). The daytime ratio R_1 is lower than it is at night because of the lack of photochemical reactions, thus a longer HO_2 lifetime at night. The high proportion of RO_2+NO during night is due to high [NO] at dawn.

The RO_2 concentration is also important when evaluating the impact of HO_2 uptake. Using the modeled value of RO_2 concentration in Wangdu campaign, a higher proportion of HO_2 uptake to about 21% of ROx sinks in daytime can be calculated. However, using the modified field measured RO_2 concentration in Wangdu campaign, HO_2 uptake is less important in the budget of ROx as shown in Fig (4 c), which is in line with the results from Tan et al. (2020).

4 Summary and conclusions

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

The interaction between organics and soluble copper and the influence of organics on aerosol properties will lead to further uncertainty in the calculation of the uptake coefficient. Lakey et al. (Lakey et al., 2016a;Lakey et al., 2015;Lakey et al., 2016b) have also shown that the addition of an organic compound to Cu^{2+} doped aerosols such as oxalic acid, which forms oxalate ions $(C_2O_4)^{2-}$ in the aerosol, results in a lower value of γ_{HO_2} as such ions forms a complex with the TMI.

Taketani et al. collected the filter samples of aerosol in Mts. Tai and Mts. Mang, North China (Taketani et al., 2012) and re-aerosolized from the water extracts of sampled particles. The measured uptake coefficients for Mt. Tai samples ranged between 0.09 and 0.40, while those at Mt. Mang were between 0.13 and 0.34. Li et. al (Li et al., 2019b) suggest that the rapid decrease of $PM_{2.5}$ in China has slowed down the reactive uptake rate of HO_2 radicals by aerosol particles and could have been themain reason for the increase in ozone in the North China Plain in the recent years. They apply a value of the uptake coeffient of of 0.2 in their model calculations. However, the results of the MARK model and of the empirical equation in this paper suggest that the HO_2 uptake coefficient could be smaller and highly variable for typical conditions in the North China Plain. Further research is needed to study the effects of heterogeneous uptake of HO_2 on gas phase and heterogeneous physico-chemical reactions under different environmental conditions in different regions.

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

Author Contribution

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

Competing Interest

The authors have no conflict of interests.

Data Availability

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

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