



# Influence of aerosol copper on HO<sub>2</sub> uptake: a novel parameterized equation

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Received: 5 March 2020 – Discussion started: 24 March 2020

Revised: 25 October 2020 – Accepted: 26 October 2020 – Published: 19 December 2020

**Abstract.** Heterogeneous uptake of hydroperoxyl radicals (HO<sub>2</sub>) onto aerosols has been proposed to be a significant sink of HO<sub>x</sub>, hence impacting the atmospheric oxidation capacity. Accurate calculation of the HO<sub>2</sub> uptake coefficient  $\gamma_{\text{HO}_2}$  is key to quantifying the potential impact of this atmospheric process. Laboratory studies show that  $\gamma_{\text{HO}_2}$  can vary by orders of magnitude due to changes in aerosol properties, especially aerosol soluble copper (Cu) concentration and aerosol liquid water content (ALWC). In this study we present a state-of-the-art model called MARK to simulate both gas- and aerosol-phase chemistry for the uptake of 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 and new laboratory data included in this work. This new parameterization will be applicable to wet aerosols, and it will complement current IUPAC recommendations. The new parameterization is as follows (the explanations for symbols are in the Appendix):

$$\frac{1}{\gamma_{\text{HO}_2}} = \frac{1}{\alpha_{\text{HO}_2}} + \frac{3 \times \nu_{\text{HO}_2}}{4 \times 10^6 \times R_d H_{\text{corr}} RT \times (5.87 + 3.2 \times \ln(\text{ALWC}/[\text{PM}] + 0.067)) \times [\text{PM}]^{-0.2} \times [\text{Cu}^{2+}]_{\text{eff}}^{0.65}} + \frac{\nu_{\text{HO}_2} l}{4 R T H_{\text{org}} D_{\text{org}} \varepsilon}.$$

All parameters used in the paper are summarized in Table A1. Using this new equation, field data from a field campaign were used to evaluate the impact of the HO<sub>2</sub> uptake onto aerosols on the RO<sub>x</sub> (= OH + HO<sub>2</sub> + RO<sub>2</sub>) budget. Highly variable values for HO<sub>2</sub> uptake were obtained for the North China Plain (median value < 0.1).

## 1 Introduction

The atmospheric cleaning capacity of the troposphere is largely determined by the concentrations of the hydroxyl radical, which are closely linked with the concentrations of

the hydroperoxyl (HO<sub>2</sub>) radical. In the established chemical mechanism, the coupling of OH and HO<sub>2</sub> is strongly determined by the reaction of OH + VOCs (volatile organic compounds) / CO / HCHO / CH<sub>4</sub> / H<sub>2</sub> / SO<sub>2</sub> and HO<sub>2</sub> + 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<sub>2</sub> under some conditions such as low NO (Tang et al., 2017). For high aerosol mass load, the reaction rate of HO<sub>2</sub> with aerosol particles could be fast enough to influence the concentration of HO<sub>x</sub> radicals and, consequently, reduce ozone production from HO<sub>2</sub> + NO (Kanaya et al., 2009; Li et al., 2019b).

From a global perspective, the impact of HO<sub>2</sub> uptake on the calculated HO<sub>x</sub> concentrations is diagnosed to be about 10 %–40 % (Jacob, 2000; Whalley et al., 2015, 2010; Mao et al., 2010; Li et al., 2019b, a), and often the value of  $\gamma_{\text{HO}_2}$  (the heterogeneous uptake coefficient; Schwartz, 1984, 1986) is assumed to be a single value, 0.2 (Tie et al., 2001; Martin et al., 2003). The model results of HO<sub>2</sub> uptake influence are lowered when a parameterized equation of  $\gamma_{\text{HO}_2}$  is used without considering the influence of transition metal ions (TMIs) (Thornton et al., 2008). The reasons for the lower reactivity in the absence of TMIs include the lower reaction rate of aqueous HO<sub>2</sub> / O<sub>2</sub><sup>−</sup> reactions (Thornton et al., 2008). However, in spite of the lower HO<sub>2</sub> uptake coefficient used, a significant impact on the calculated [OH] and O<sub>3</sub> production rate is suggested for air masses over the areas of Chinese megacities (Macintyre and Evans, 2011). A model study (Xue et al., 2014) considering the aerosol uptake of HO<sub>2</sub> showed an impact on the simulated HO<sub>2</sub> concentrations and local O<sub>3</sub> production rates in Chinese urban regions: Beijing, Shanghai, and Guangzhou. Furthermore, researchers have proposed that in the North China Plain (Li et al., 2019a, b), the reduced HO<sub>2</sub> uptake owing to reduction of the 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  $\gamma_{\text{HO}_2}$ .

Previous studies show that the value of  $\gamma_{\text{HO}_2}$  from the laboratory, field, and modelling 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  $\gamma_{\text{HO}_2}$  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<sub>2</sub> with soluble Cu ions may be fast enough; thus the uptake coefficient is limited by the mass accommodation coefficient  $\alpha$ . Due to the widespread distribution of Cu<sup>2+</sup> ions in ambient particles, the absence of an accurate evaluation of  $\gamma_{\text{HO}_2}$  is one of the largest uncertainties for the determination of the impact of HO<sub>2</sub> uptake on pressing atmospheric issues such as ozone formation.

In this study, we reanalysed several datasets of the aerosol uptake of HO<sub>2</sub> from laboratory studies reported in the lit-

erature and a new dataset of the HO<sub>2</sub> uptake coefficient on Cu-doped ammonium sulfate aerosols at 43 % relative humidity as well as proposing a novel parameterized equation (abbreviated as NEq. in the paper) for the prediction of  $\gamma_{\text{HO}_2}$  that best fits all the laboratory results. Furthermore, for the Wangdu field campaign, we also calculated  $\gamma_{\text{HO}_2}$  according to the NEq. and the impact of HO<sub>2</sub> uptake on HO<sub>x</sub> (=OH + HO<sub>2</sub>) budget was evaluated.

## 2 Materials and methods

### 2.1 The model

A Multiphase Reaction Kinetic (MARK) model is developed in this study for the simulation of  $\gamma_{\text{HO}_2}$  for the laboratory experiments. The reaction mechanism and reaction rate constants are summarized in Tables S1–S4 in the Supplement. The MARK model is currently capable of simulating inorganic deliquescent aerosol at ambient pressure and temperature. The model directly calculates the averaged quasi-first-order gas-phase HO<sub>2</sub> uptake loss rate at steady state,  $k_{\text{het}}$  (s<sup>−1</sup>) in Eq. (1).  $\gamma_{\text{HO}_2}$  is retrieved by Eq. (2), considering the influence of the aerosol liquid water content (ALWC) (g cm<sup>−3</sup>) rather than surface density because of the influence of the RH on the uptake process (Kuang et al., 2018; Bian et al., 2014).

$$\frac{d[\text{HO}_2]}{dt} = -k_{\text{het}} \times [\text{HO}_2] \quad (1)$$

$$k_{\text{het}} = \left( \frac{R_d}{D_g} + \frac{4}{\gamma v_{\text{HO}_2}} \right)^{-1} \times \frac{3\text{ALWC}}{\rho R_d} \quad (2)$$

The meanings of the symbols are summarized in the Appendix. The units of aqueous reagents are converted to molec cm<sup>−3</sup> in the model by  $k_{\text{mt}}$ . To combine both gas-phase molecular diffusion and liquid-phase interface mass transport processes, the approach adopted uses one variable called  $k_{\text{mt}}$  (Schwartz, 1984, 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  $k_{\text{mt}}$  is given by Eq. (3):

$$k_{\text{mt}} = \left( \frac{R_d^2}{3D_g} + \frac{4R_d}{3v_{\text{HO}_2}\alpha} \right)^{-1}. \quad (3)$$

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  $k_{\text{mt}X} \times \text{ALWC}$  (where  $X$  is the reactant molecule). Moreover, the conversion rate of aqueous-phase reactants to the gas phase can be calculated as  $\frac{k_{\text{mt}X}}{H^{\text{cc}} \times RT}$ . The unit of  $k_{\text{mt}}$  is s<sup>−1</sup>, as  $k_{\text{mt}}$  contains the conversion from m<sub>air</sub><sup>−3</sup> of the gas-phase molecule concentrations to m<sub>aq</sub><sup>−3</sup> of the aqueous-phase molecule concentrations and in

the other direction. For larger particles (radius > 1 µm),  $k_{\text{mt}}$  is mainly determined by the gas-phase diffusion of HO<sub>2</sub>. For smaller particles (radius < 1 µm),  $k_{\text{mt}}$  is mainly determined by the accommodation process. The MARK model can simultaneously simulate gas and liquid two-phase reaction systems in the same framework.

The aerosol particle condensed phase is not an ideal solution. Consequently, the effective Henry's law constant  $H^{\text{cc}}$  should be applied in the model calculation that takes into account the effects of solution pH and the salting out effect in the small gas-phase molecule (such as HO<sub>2</sub>, OH, and O<sub>2</sub>) due to the existence of electrolytes in the solution (Ross and Noone, 1991). This study uses the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007) to calculate the ALWC and components' concentrations for metastable deliquescent aerosols. The effective Cu<sup>2+</sup> 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 $\gamma_{\text{HO}_2}$ 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  $I$ .  $H_0$  is estimated to be about 3900 M atm<sup>-1</sup> at 298 K for HO<sub>2</sub> (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>, last access: 30 November 2020).  $H_0$  should be corrected by the solution pH and the salting out effect. In the MARK model, these two corrections are incorporated as  $H^{\text{cc}}$ :

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

The activity coefficient  $A$  for HO<sub>2</sub> and other neutral small molecules such as H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> can be expressed as (Ross and Noone, 1991)

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

According to this correction,  $H^{\text{cc}}$  of HO<sub>2</sub> increases with RH. The ratio of  $H^{\text{cc}}$  to  $H_0$  ranges from 0.03 (40 % RH,  $I = 16.7$ ) to 0.34 (80 % RH,  $I = 5.5$ ). Although the salting effect and the ionic strength are mainly driven by [NH<sub>4</sub><sup>+</sup>] and

(SO<sub>4</sub><sup>2-</sup>), ionic strength increases quickly from 5.9 to 9.5 with (Cu<sup>2+</sup>) from 0.1 to 1 M and limits the solubility of HO<sub>2</sub> gas molecules.

### 2.2.2 Aerosol particle condensed-phase Cu<sup>2+</sup> 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 vapour. The salts in the metastable aerosol are all dissolved in the aqueous phase. For metastable aerosols, this paper uses thermodynamic models to calculate ALWC and aerosol particle condensed-phase component concentrations. In this work the ISORROPIA II (Fountoukis and Nenes, 2007; Capps et al., 2012) thermodynamic equilibrium model for inorganic aerosol systems is used to take this into account.

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 the calculation of aerosol chemistry. The ion activity coefficient refers to the effective concentration of ions participating in an electrochemical reaction in an electrolyte solution.

Since there is no direct evidence of the existence of Cu/Fe redox reactions of HO<sub>2</sub> which produce H<sub>2</sub>O rather than H<sub>2</sub>O<sub>2</sub> as proposed by Mao et al. (2013), in the scope of this paper, HO<sub>2</sub> uptake produces H<sub>2</sub>O separately by Cu- and Fe-free ions as proposed by many research studies (Mozurkewich et al., 1987; Hanson et al., 1992; Thornton and Abbatt, 2005; Thornton et al., 2008; Taketani et al., 2009; Macintyre and Evans, 2011). Fe-free ions can be seen as the equivalent Cu-free ions in the application of the MARK model or the parameterized equation mentioned below.

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

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

where  $D$  is given by Eq. (7):

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

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

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

where  $\varepsilon(xyI)$  denotes “interaction coefficients”, and the summation extends over all ions ( $y$ ) in the solution at a molality of  $m_y$ . For ions of similar charge,  $\varepsilon(xyI)$  is set to zero. For ions of unequal charge,  $\varepsilon(xyI)$  may be calculated from the logarithm solution mean activity coefficient

$\log(A_{\pm})$  (Clegg et al., 1998) of the single electrolyte at the same  $I$  according to Eq. (9):

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

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

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

In the aerosol particle condensed phase, an effective concentration rather than the total concentration of the Cu ions should be calculated in catalytic aqueous reactions with HO<sub>2</sub>. The effective concentration of TMIs can be calculated as

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

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

### 2.2.3 The conversion formula of $[\overline{\text{HO}_2}]$ and $\text{HO}_{2(r)}$

Gas-phase HO<sub>2</sub> molecules dissolve in the particle condensed phase and diffuse from the surface of a particle toward the centre in parallel with aqueous-phase reactions. We need to evaluate  $[\overline{\text{HO}_2}]$ , the assumed averaged steady-state HO<sub>2</sub> concentration over the volume of the particle.  $[\text{HO}_{2(r)}]$  is HO<sub>2</sub> concentration at the surface of particles. The ratio of these two concentrations can be calculated as (Schwartz, 1986, 1984)

$$\frac{[\overline{\text{HO}_2}]}{[\text{HO}_{2(r)}]} = 3 \times \left( \frac{\coth(q)}{q} - \frac{1}{q^2} \right), \quad (12)$$

where  $q$  is given by Eq. (13):

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

and  $D_{\text{aq}}$  is the aqueous-phase diffusion coefficient [ $\text{cm}^2 \text{s}^{-1}$ ],  $k_{\text{eff}}$  is the comprehensive liquid-phase reaction rate coefficient which encompasses both HO<sub>2</sub> dissolution equilibrium reactions and liquid-phase chemical-physical reactions during HO<sub>2</sub> uptake process.  $k_{\text{eff}}$  is calculated by Eq. (19) and includes the influence of the salting out effect of HO<sub>2</sub> and the ionic strength effects on TMIs.  $k_{\text{eff}}$  will change dramatically according to the concentration of equivalent copper ions and the diameter of particles. Higher Cu concentration will make the ratio smaller and cause larger uncertainties, however, in the copper-doped aerosol particle, because of the high value of  $k_{\text{eff}}$  (typical value is  $2.9 \times 10^6 \text{ M s}^{-1}$  with  $1 \text{ M Cu}^{2+}$  and  $3.25 \times 10^4 \text{ M s}^{-1}$  with  $0.001 \text{ M Cu}^{2+}$ ) and small count median diameter ( $R_d$ ) (usually smaller than  $1 \mu\text{m}$ ), the ratio

$\frac{[\overline{\text{HO}_2}]}{[\text{HO}_{2(r)}]}$  is close to 1. At a diameter of 100 nm, and a relative humidity between 40 % and 90 %, the condensed-phase copper ion concentration varies from  $10^{-5}$  to 1 M, the average ratio of the surface HO<sub>2</sub> concentration and the condensed-phase HO<sub>2</sub> concentration is beyond 0.87 at every Cu concentration. The ratios are calculated by simulation of  $k_{\text{eff}}$  and the accordingly calculations by Eqs. (12) and (13). Thus, in this model, we assume the surface concentration of HO<sub>2</sub> equals to the condensed-phase average HO<sub>2</sub> concentration.

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

The accommodation coefficient of HO<sub>2</sub> ( $\alpha_{\text{HO}_2}$ ) is independent of the concentrations of Cu-free ions if the viscosity of particles is maintained, while the more accurate accommodation coefficient can only be measured with no limitation of the aqueous mass transfer flux; in this situation,  $\alpha_{\text{HO}_2}$  is equal to  $\gamma_{\text{HO}_2}$ . HO<sub>2</sub> uptake coefficients are summarized for copper-doped inorganic aerosol particles from various previous laboratory studies. The uptake coefficient of HO<sub>2</sub> is approximately 0.5 for sulfate aerosol and even higher for chlorine or nitrate aerosol because of the catalytic effect of  $\text{Cu}^{2+}$  on aqueous HO<sub>2</sub> / O<sub>2</sub><sup>−</sup> (Table 1). In this situation, the aqueous reactions are fast enough for the uptake process to be limited primarily by the mass transport process (accommodation), and the uptake coefficient is equal to the accommodation coefficient. Thus, the MARK model typically uses  $\alpha_{\text{HO}_2}$  of 0.5. We also tested the influence of the accommodation coefficient on the calculated HO<sub>2</sub> uptake coefficient in a field campaign; for details, please see the Supplement.

### 2.4 The experimental setup and methodology of the latest results of $\gamma_{\text{HO}_2}$

In this study, we also included the latest results which were measured at Leeds. The experimental setup and methodology used to make the new measurements of  $\gamma(\text{HO}_2)$  reported here have been described in detail elsewhere (Moon et al., 2018; Lakey et al., 2016b; George et al., 2013), and so only brief details are given here. In summary, the experiments were performed by moving an HO<sub>2</sub> injector backwards and forwards along the concentric axis of a laminar aerosol flow tube, hence changing the contact time between HO<sub>2</sub> and the aerosols. Measurements of  $[\text{HO}_2]$  were performed using laser-induced fluorescence (LIF) spectroscopy at low pressure (the fluorescence assay by gas expansion (FAGE) technique (Heard and Pilling, 2003)), and the total aerosol surface area was determined with a Scanning Mobility Particle Sizer (SMPS) at the end of the flow tube. Aerosol particles were produced using a constant output atomizer (TSI, 3076), and the aerosol concentration and hence surface area could be varied, being controlled using a high-efficiency particulate air (HEPA) filter in a bypass arrangement. Atomizer solutions were prepared by dissolving 0.01 mol of am-

**Table 1.**  $\gamma_{\text{HO}_2}$  determined under laboratory conditions for copper-doped inorganic aerosols.

| Aerosol type                                    | RH (%)    | Estimation of [Cu]<br>in aerosol (mol L <sup>-1</sup> ) | $\gamma_{\text{HO}_2}$ | Ref.                       |
|-------------------------------------------------|-----------|---------------------------------------------------------|------------------------|----------------------------|
| NH <sub>4</sub> HSO <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            | Lahey et al. (2016b)       |
| (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 (M).

monium sulfate (AS) (Fisher Scientific, > 99 %) with varying amounts of copper (II) sulfate (Fisher Scientific, > 98 %) in 500 mL of Milli-Q water. The data were analysed as described in George et al. (2013). The pseudo-first-order loss rate coefficient ( $k'$ ) was obtained from the gradient of a plot of  $\ln(\text{HO}_2 \text{ signal})$  against the interaction time between HO<sub>2</sub> and the aerosol before sampling by the FAGE detector. The uptake coefficient ( $\gamma(\text{HO}_2)$ ) was obtained from the linear least-squares gradient of the plot of  $k'$  against the surface area concentration of aerosols in the flow tube. The error given on all measurements of  $\gamma(\text{HO}_2)$  represents  $2\sigma$  of the uncertainty of the fitted gradient. A correction to  $k'$  was applied to take into account non-plug flow conditions in the flow tube using the Brown method.

### 3 Results and discussion

#### 3.1 Parameter sensitivity analysis of the MARK model

Hygroscopic inorganic particles are one of the most important components of PM<sub>2.5</sub> in ambient air. The annual average contribution of inorganic aerosol to PM<sub>2.5</sub> is between 25 % and 48 % across China (Tao et al., 2017), especially NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and other inorganic ions. In laboratory studies of radical heterogeneous reactions, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol is most widely studied because of its simple components and its easy way of being generated and because it is an important component of urban aerosols (Cheng et al., 2012; Yin et al., 2005). A simplified approach was used to explore the mechanism of HO<sub>2</sub> heterogeneous uptake to derive a parameterized equation for the uptake coefficient,  $\gamma_{\text{HO}_2}$ .

In this study, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol uptake reactions of HO<sub>2</sub> are simulated by the MARK model, and good correlation between simulation results and experimental results is obtained, especially considering the influence of both [Cu<sup>2+</sup>] and RH (for the lack of measured data the parameterized equation is only valid in the range of 40 % to 90 % RH).

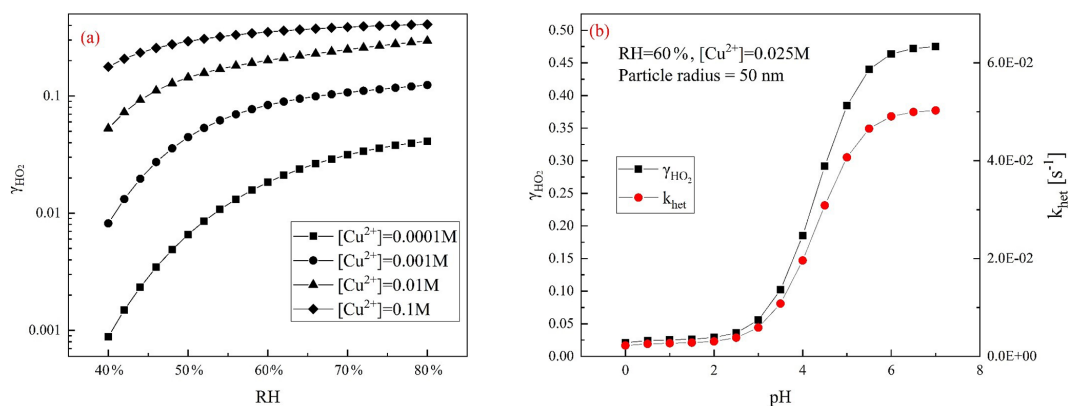
Figure 1 shows the influences of both factors, RH and condensed-phase pH together with Cu<sup>2+</sup> concentration, on the heterogeneous process of HO<sub>2</sub>. As the RH rises, the  $\gamma_{\text{HO}_2}$  exhibits a logarithmic growth. Higher RH means a higher water content, which dilutes the bulk-phase ions and thus promotes the activity coefficients of reactant ions in the aerosol particle condensed phase and the solubility of gas-phase reactants such as OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>.

$\gamma_{\text{HO}_2}$  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 (pK<sub>a</sub> = 4.7) and has a low solubility in an acidic environment. The higher condensed-phase pH is favourable 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). 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 an increase of condensed-phase pH because in an alkaline environment HO<sub>2</sub> is more dissociated to O<sub>2</sub><sup>-</sup>, which has a quicker reaction rate with Cu<sup>2+</sup> / Cu<sup>+</sup>. The pH of the ambient atmospheric aerosol is measured to be generally below 5, even when the concentration of NH<sub>3</sub> is high as in Beijing and Xi'an (Ding et al., 2019; Guo et al., 2017) with a range of 3–5. In this range,  $\gamma_{\text{HO}_2}$  is highly affected by aerosol condensed-phase pH, mainly because of the change of HO<sub>2</sub> solubility.

#### 3.2 Model validation

Although the MARK model simulation results in this paper are not obtained by adjusting parameters to fit the experimental data points, the MARK model fitted well with these results under different ambient RH and Cu<sup>2+</sup> concentrations.

At present, there are experimental measurements of  $\gamma_{\text{HO}_2}$  at different RHs (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), but there is no systematic experimental study of this dependence,



**Figure 1.** Influence of various parameters upon  $\gamma_{\text{HO}_2}$  predicted by the MARK model. (a)  $\gamma_{\text{HO}_2}$  increases with the RH at different  $[\text{Cu}^{2+}]$ ; (b)  $\gamma_{\text{HO}_2}$  denoted by black squares and black line and  $k_{\text{het}}$  in red circles and red line increase with aerosol particle condensed-phase pH.

where only RH is changed and not other parameters. Many research studies proposed that  $\gamma_{\text{HO}_2}$  is higher for aqueous inorganic aerosol than for dry inorganic aerosol. Although previous experiments did not directly measure the dependence of RH, the change of the uptake coefficient met the simulation trend (see Fig. 2). For hygroscopic inorganic aerosols, RH significantly affects the aerosol liquid water content, changing its ionic strength, aqueous reagent activity coefficients, and the solubility of gas-phase reactants such as OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>.

Aerosol condensed-phase copper ion concentration is another important factor of HO<sub>2</sub> uptake by adjusting the aqueous reaction rates between HO<sub>2</sub> / O<sub>2</sub><sup>−</sup> and Cu. As shown in Fig. 2, when the condensed-phase copper ion concentration is less than  $1\text{--}2 \times 10^{-4}\text{ M}$ , the heterogeneous uptake of HO<sub>2</sub> is not significant and may mainly be driven by the self-reaction of HO<sub>2</sub>. This threshold is consistent with the results of previous research studies (Mozurkewich et al., 1987; Lakey et al., 2016b). The threshold is also consistent in different heterogeneous media of aerosol and cloud or rain droplets. As the copper concentration increases, the solution ionic strength increases, and  $\gamma_{\text{HO}_2}$  rapidly rises to the limit of the accommodation coefficient and the limitation of the HO<sub>2</sub> solubility.

What is more, laboratory measurement uncertainties will directly influence the evaluation of the deviation between the modelled HO<sub>2</sub> uptake coefficient and the measured results because all the parameters inputted in the MARK model are in reference to the measurement conditions. However, it is difficult to calculate the detailed uncertainties from all factors that influence  $\gamma_{\text{HO}_2}$  because of the non-linear reaction system. Uncertainties of the experimental conditions such as RH and particle diameters are combined into the reported values of  $\gamma_{\text{HO}_2}$ . Taking all these into account, we calculated an averaged uncertainty for the experimental values of  $\gamma_{\text{HO}_2}$  in different ranges of Cu ion concentration. Laboratory measurement uncertainty has the largest value of 35.1 % in the range of  $1 \times 10^{-4}$  to 0.01 M soluble copper concentration, 14.9 %

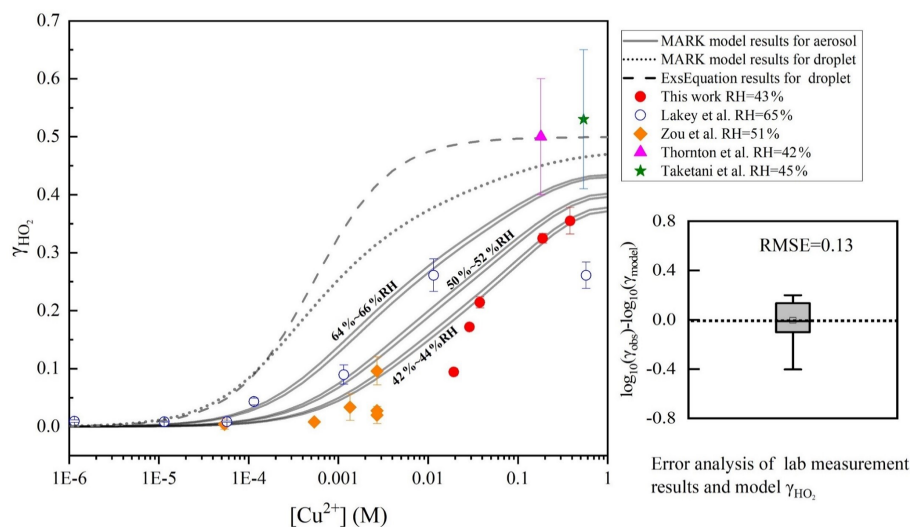
below  $1 \times 10^{-4}\text{ M}$ , and 9.3 % higher than 0.01 M. In general, good agreement is achieved between the MARK model results and the results of the previous laboratory studies, which were also classified based on a statistical parameter, the root mean square error (RMSE) (Fig. 2). In this paper, the relative error of each measured data point is considered to calculate the weighted average in RMSE:

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

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

### 3.3 Comparison of the classical parameterized equation and the MARK model

The classical parameterized equation (CEq.) (Thornton et al., 2008; Hanson et al., 1992, 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>, last access: 30 November 2020) proposed for the HO<sub>2</sub> uptake of deliquesced aerosol particles has been proved to provide good estimation of the reactive gas molecular uptake coefficient on dilute solution droplets (Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller



**Figure 2.** Dependence of  $\gamma_{\text{HO}_2}$  on aerosol copper concentration. Red filled circles denote the results at 43 % RH measured at Leeds included in this paper. Blue hollow circles at 65 % RH (Lakey et al., 2016b). Yellow filled diamonds denote results at 51 % RH (Zou et al., 2019), filled purple triangle at 42 % RH (Thornton and Abbatt, 2005), and filled green star at 45 % RH (Taketani et al., 2008). The dashed grey line denotes the results of the classical parameterized equation (named CEq. in this paper)  $\gamma_{\text{HO}_2}$  with deliquesced aerosol particles (Thornton et al., 2008; Hanson et al., 1992, 1994; Jacob, 2000; Kolb et al., 1995), which was confirmed by research studies of reactive gas molecular uptake on dilute solution droplets (Magi et al., 1997) and on aqueous surfaces (Utter et al., 1992; Müller and Heal, 2002; Hu et al., 1995). The solid grey lines represent the model results of the MARK model in this study at various RHs (two lines represent the range of RH from 64 % to 66 %, 50 % to 52 %, and 42 % to 44 %), and the short dotted line represents the result in the MARK model of HO<sub>2</sub> with dilute solution droplets. The root mean square error (RMSE) between the MARK modelled values and the full dataset is 0.13. The aerosol pH is set as 4.5 based on the aqion 7.0.8 interface, considering the participation of Cu ions (for details, please see <https://www.aqion.de/>, last access: 30 November 2020).

and Heal, 2002; Hu et al., 1995).

$$\frac{1}{\gamma_{\text{HO}_2}} = \frac{1}{\alpha_{\text{HO}_2}} + \frac{\nu_{\text{HO}_2}}{4H_{\text{corr}}RT\sqrt{D_{\text{aq}}k_{\text{TMI}}[\text{TMI}]}\left[\coth\left(\frac{R_d}{l_{\text{rd}}} - \left(\frac{l_{\text{rd}}}{R_d}\right)\right)\right]} \quad (15)$$

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

When the classical parameterized equation (CEq.) is applied to the calculate HO<sub>2</sub> uptake coefficient with copper-doped aerosol, CEq has a higher deviation of  $\gamma_{\text{HO}_2}$  between the measured results compared to the MARK model. All input parameters are the same, except that the MARK model involved more liquid-phase reactions instead of only considering the second-order rate coefficient ( $k_{\text{TMI}}$ ) of HO<sub>2</sub> and O<sub>2</sub><sup>−</sup> with transition metal ions as the CEq. did.  $k_{\text{TMI}}$  is the most important parameter in the calculation of the uptake coefficient. Based on the research by Bielski et al. (1985), we used the effective rate constant of HO<sub>2</sub><sub>total</sub> (=HO<sub>2</sub>(aq) + O<sub>2</sub><sup>−</sup>(aq)) with Cu ions as  $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  rather than the more commonly used value of  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  considering the pH limitation (pH is about 3–5 in the ambient aerosol particle condensed phase as discussed above). The prior value ( $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) reflects the rate of reaction between HO<sub>2</sub>

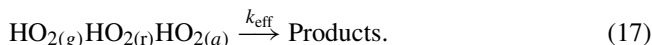
and Cu<sup>2+</sup>, more prevalent in acidic aerosol such as ammonium sulfate, and the latter ( $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) between O<sub>2</sub><sup>−</sup> and Cu<sup>2+</sup> ions, which is more prevalent in aerosols with a pH greater than the pK<sub>a</sub> of HO<sub>2</sub>, such as NaCl (Bielski et al., 1985). This treatment within the calculation can bring predictions more in line with experimental results in the CEq., as shown by the dashed line in Fig. 2.

IUPAC (Ammann et al., 2013; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>, last access: 30 November 2020) proposed the effective rate coefficient  $k^1$  for the reaction of HO<sub>2</sub><sub>total</sub> (=HO<sub>2</sub>(aq) + O<sub>2</sub><sup>−</sup>(aq)) with Cu ions as  $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  to achieve the best fit based on the calculation results from Lakey et al. (2016b). The low reaction rates used here in the CEq. are assumed to likely result from the combined effects of solute strength effects as discussed by Lakey et al. (2016b). The MARK model uses the same framework with the CEq and considers the Setchenov salting out and ionic strength effects on HO<sub>2</sub> uptake more comprehensively and in more detail and proposes  $k_{\text{eff}}$  as the effective reaction coefficient (Eq. 19). Considering the small RMSE between the MARK model and the laboratory studies, we proposed a novel parameterized equation (NEq.) to better describe the influence of [Cu<sup>2+</sup>] and RH on  $\gamma_{\text{HO}_2}$ .



### 3.4 A novel parameterized equation of $\gamma_{\text{HO}_2}$

When the full reaction system reaches steady state, the reaction of HO<sub>2</sub> in the aqueous particle phase can be expressed as the following reaction scheme (Schwartz, 1984, 1987; Schwartz and Freiberg, 1981):



Gas-phase HO<sub>2(g)</sub> molecules transport onto the surface of the aerosol particles; HO<sub>2(r)</sub> then dissolves in the condensed phase to give HO<sub>2(a)</sub>. The reactions between Cu<sup>2+</sup>/Cu<sup>+</sup> and HO<sub>2</sub> can be seen as catalytic reactions because in the model simulations, the total amount of [Cu<sup>2+</sup>] + [Cu<sup>+</sup>] does not change with reaction time. The rate of HO<sub>2</sub> aqueous reaction with copper ions is noted as  $k_{\text{eff}}$ . For fine particles, we can safely assume that the interface concentration [HO<sub>2(r)</sub>] is equal to the condensed-phase average  $\bar{[\text{HO}_2]}$  concentration due to rapid diffusion in the liquid phase (details have been discussed in Sect. 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  $\gamma = \alpha(1 - \frac{c_{\text{a,surf}}}{H^{cc}c_{\text{g,surf}}})$ , where  $c_{\text{a,surf}}$  is the surface concentration of the reactant, and  $c_{\text{g,surf}}$  is the gas-phase concentration. In the process of HO<sub>2</sub> uptake, we deduce the parameterized equation (NEq.) of  $\gamma_{\text{HO}_2}$  in the framework of the resistance model:

$$\frac{1}{\gamma} = \frac{1}{\alpha_{\text{HO}_2}} + \frac{3 \times v_{\text{HO}_2}}{4 \times R_d \times H_{\text{corr}} \times RTk_{\text{eff}}} \quad (18)$$

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

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

From Eq. (18), it can be deduced that  $\gamma_{\text{HO}_2}$  can be calculated by optimizing  $k_{\text{eff}}$  under different ambient environmental conditions from the MARK model results. The MIPFIT model (Markwardt, 2009; Lewis et al., 2009) in the IDL software program is used to optimize  $k_{\text{eff}}$  using the Levenberg–Marquardt algorithm. Because the equation is empirical, the initial value of  $k_{\text{eff}}$  is set as 1.  $k_{\text{eff}}$  is related to [Cu<sup>2+</sup>]<sub>eff</sub>, which is the sum of condensed-phase soluble copper concentration and other equivalent copper concentrations mentioned (Eq. 11). The exponent of [Cu<sup>2+</sup>]<sub>eff</sub> 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.  $f(\text{ALWC}, [\text{PM}])$  has a negative exponential relationship to [PM] and has a positive linear relationship to RH.

We further calculated the RMSE of the modelled data and NEq. (Eq. 15) data under different RH conditions. The range of values shows the difference between the modelled data and NEq. data at different Cu<sup>2+</sup> concentrations. At low RH and

consequently relatively low ALWC,  $\gamma_{\text{HO}_2}$  is more sensitive to [Cu<sup>2+</sup>], especially at low [Cu<sup>2+</sup>]. This sensitivity cannot be fully represented in the parameterized equation. What is more, at low [Cu<sup>2+</sup>] and low RH, the value of  $\gamma_{\text{HO}_2}$  is smaller than in other conditions, so the uncertainty of  $\gamma_{\text{HO}_2}$  becomes larger.

All the RMSE values are smaller than 0.2, which indicates a minor deviation from the laboratory results in our  $\gamma_{\text{HO}_2}$  equation. In the typical ambient urban atmospheric environment, with an aerosol mass concentration of 10–300 µg m<sup>-3</sup>, aqueous Cu<sup>2+</sup> concentration of 10<sup>-5</sup>–1 molar concentration, and a relative humidity between 40 %–90 %, the NEq. can be used. Beyond this range, the application of the NEq. may cause a large deviation. The HO<sub>2</sub> uptake under dry conditions needs further investigation in the future, but it is probably not of high priority because the effective reaction volume becomes 10 % or less of the aerosol volume for dry conditions, and the HO<sub>2</sub> 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).

### 3.5 Evaluation of the impact of the new HO<sub>2</sub> uptake parameterization in the Wangdu campaign

Many model studies (Lakey et al., 2015; Martinez et al., 2003; Tie et al., 2001; Whalley et al., 2015) suggest that the heterogeneous uptake of HO<sub>2</sub> radicals affects the global distribution of trace gases and the atmospheric oxidant capacity, especially in regions with high aerosol loading or low NO<sub>x</sub> 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<sub>2</sub> 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 at a rural site (Wangdu) in the North China Plain (Tan et al., 2020), the HO<sub>2</sub> uptake coefficient and the ratios of the HO<sub>2</sub> uptake loss rates (TR<sub>HO<sub>2</sub>uptake</sub>) to the sum of the RO<sub>x</sub> termination rates (TR<sub>RO<sub>x</sub>sinks</sub>) are calculated with direct measurements of the RO<sub>x</sub> radicals, trace gas species, ALWC, and the aerosol condensed-phase component concentrations (please see the Supplement for details). The experimental determined RO<sub>x</sub> termination rates include reaction channels from OH + NO<sub>2</sub>, OH + NO, HO<sub>2</sub> + HO<sub>2</sub>, HO<sub>2</sub> + RO<sub>2</sub>, and RO<sub>2</sub> + NO. Considering the solubility and size distribution of particle metal copper (Fang et al., 2017; Hsu et al., 2010a; Mao et al., 2013), we can estimate  $\gamma_{\text{HO}_2}$  in the daytime and night-time.



**Table 2.** Average daytime results of observed meteorological parameters and trace gas concentration in the Wangdu campaign from 10 June to 6 July 2014.

| Parameters            | Average values | 1 $\sigma$ accuracy |
|-----------------------|----------------|---------------------|
| Temperature (°C)      | 27 $\pm$ 4     | $\pm$ 0.05 %        |
| Pressure (hPa)        | 1000 $\pm$ 5   | $\pm$ 0.05 %        |
| RH (%)                | 61 $\pm$ 18    | $\pm$ 0.05 %        |
| O <sub>3</sub> (ppb)  | 55.6 $\pm$ 9.0 | $\pm$ 5 %           |
| NO <sub>x</sub> (ppb) | 10 $\pm$ 13.6  | $\pm$ 20 %          |
| HONO (ppb)            | 0.8 $\pm$ 0.24 | $\pm$ 20 %          |
| CO (ppm)              | 0.6 $\pm$ 0.19 | < 5 %               |
| Isoprene (ppb)        | 0.5 $\pm$ 0.11 | $\pm$ 15 %–20 %     |
| HCHO (ppb)            | 7 $\pm$ 0.69   | $\pm$ 5 %           |

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

Wangdu is located in the centre of the Beijing–Tianjin–Hebei area, and it is a regional site. The observations were carried out in the summer with serious photochemical smog pollution events (Tan et al., 2017, 2020). Table 2 summarizes the meteorological and chemical conditions in this field campaign. In terms of parameters such as temperature, pressure, and relative humidity, the Wangdu area is a high-temperature and high-humidity environment with a monsoon climate.

### 3.5.2 Calculation of soluble copper ion concentration

During this campaign, the total concentration of heavy metal ions in fine particles (smaller than 2.5  $\mu$ m) was measured using a commercial instrument based on a 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 analyse the ratio of soluble copper to total copper in the aerosol particles. For particle radii smaller than 2.5  $\mu$ m of which are the bins of aerosols that contribute most to HO<sub>2</sub> uptake, the mass fraction of Cu is about 33 % to  $\sim$ 100  $\mu$ m% compared with two other size bins in ambient aerosols (2.5–10  $\mu$ m, > 10  $\mu$ m) (Mao et al., 2013). According to previous research results, the dissolution ratio of copper in aerosol particles varies from 20 % to 70 % in different regions, the solubility being lower in smaller particles (Fang et al., 2017; Hsu et al., 2004, 2010b). Therefore, when using the NEq. to calculate the HO<sub>2</sub> 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 assume 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  $\gamma_{\text{HO}_2}$  in the Wangdu campaign.

The hourly resolution total copper concentration (ng m<sup>−3</sup>) is divided by the aerosol volume concentration and the atomic mass of copper (64) to obtain the total copper molar concentration in the aerosol (mol L<sup>−1</sup>).  $\gamma_{\text{HO}_2}$  rather depends on copper concentration, so we also evaluate the influence of copper solubility on the uptake coefficient. What is more, the unequal distribution of copper ions will also influence the HO<sub>2</sub> uptake coefficient (details in the Supplement).

### 3.5.3 $\gamma_{\text{HO}_2}$ estimated in the Wangdu field campaign

By inputting the soluble copper concentration, aerosol mass concentration, aerosol particle geometric mean diameter, and the corresponding relative humidity and temperature into the NEq., we can obtain an estimation of  $\gamma_{\text{HO}_2}$  in suburban Wangdu, which is shown in Fig. 4a and b. The time resolution is 1 h. The aerosol pH is calculated using the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007), and the averaged value is  $3.41 \pm 0.69$  ( $1\sigma$ ). The average aerosol mass concentration is  $67.2 \pm 39.7 \mu\text{g m}^{-3}$ , and the average Cu concentration is  $35.8 \pm 57.7 \text{ ng m}^{-3}$ . The fit to a Gaussian function results in a  $\gamma_{\text{HO}_2}$  value of  $0.116 \pm 0.086$  ( $1\sigma$ ) in the Wangdu campaign ( $\gamma_{\text{HO}_2}$  will increase from  $0.065 \pm 0.051$  ( $1\sigma$ ) at 10 % solubility to  $0.196 \pm 0.142$  ( $1\sigma$ ) at 70 % solubility for the summary of daytime and night-time data).

Tan et al. (2017) compared the measured and modelled OH, HO<sub>2</sub>, and RO<sub>2</sub> radicals in the Wangdu campaign. However, in this paper, they did not discuss the influence of HO<sub>2</sub> uptake. A very recent publication (Tan et al., 2020) calculated  $\gamma_{\text{HO}_2}$  in the Wangdu campaign based on the comparison of field measurement data for HO<sub>2</sub> and concentrations calculated by the box model. The paper proposes that all  $\gamma_{\text{HO}_2}$  calculated in this way from the Wangdu campaign can be fitted to a Gaussian distribution around the value of  $0.08 \pm 0.13$  ( $1\sigma$ ). This value is in the range of our estimation in this paper, considering the influence of aerosol morphology and the indirect measurement uncertainty (please see the Supplement).

The experimentally determined RO<sub>x</sub> termination rates include reaction channels from OH + NO<sub>2</sub>, OH + NO, HO<sub>2</sub> + HO<sub>2</sub>, HO<sub>2</sub> + RO<sub>2</sub>, and RO<sub>2</sub> + NO. The ratio ( $R_1$ ) of the HO<sub>2</sub> uptake loss rate ( $L_{\text{HO}_2\text{uptake}}$ ) to the whole RO<sub>x</sub> loss rate ( $L_{\text{RO}_x}$ ) is calculated by Eqs. (21) and (22).

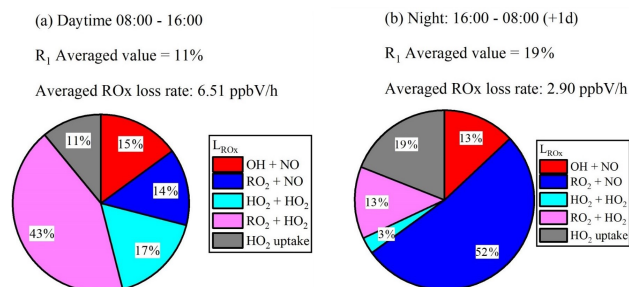
$$L_{\text{HO}_2\text{uptake}} = 0.25 \nu_{\text{HO}_2} [\text{ASA}] [\text{HO}_2] \quad (21)$$

$$R_1 = \frac{L_{\text{HO}_2\text{uptake}}}{L_{\text{RO}_x}} \quad (22)$$

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

No significant difference of  $\gamma_{\text{HO}_2}$  is observed during daytime and night-time. The HO<sub>2</sub> uptake coefficient is slightly higher at night due to the higher RH (57.6 % in the day and 67.4 % at night). However, because of the high uncertainty of the uptake coefficient, such a high trend cannot be concluded for other cases. HO<sub>2</sub> heterogeneous uptake reactions with aerosol particles have a small impact on RO<sub>x</sub> radical termination in the daytime, as shown in Fig. 4a. However, HO<sub>2</sub> uptake may be important in the termination of RO<sub>x</sub> radicals at night, shown in Fig. 4b. The daytime ratio  $R_1$  is lower than it is at night because of the lack of photochemical reactions and thus a longer HO<sub>2</sub> lifetime at night. The high proportion of RO<sub>2</sub> + NO during night-time is due to high [NO] at dawn.

The RO<sub>2</sub> concentration is also important when evaluating the impact of HO<sub>2</sub> uptake. Using the modelled value of RO<sub>2</sub> concentration in the Wangdu campaign, a higher proportion



**Figure 3.**  $R_1$  calculated by the NEq. Pie charts show the values of  $R_1$  and the loss rates for RO<sub>x</sub> during daytime (a) and night-time (b). The averaged daytime (08:00–16:00) RO<sub>x</sub> radical loss rate is  $6.5 \text{ ppbV h}^{-1}$ , and that for night-time (16:00–08:00 (+1 d)) is  $2.9 \text{ ppbV h}^{-1}$ .

of HO<sub>2</sub> uptake to about 21 % of RO<sub>x</sub> sinks in the daytime can be calculated. However, using the modified field measured RO<sub>2</sub> concentration in the Wangdu campaign, HO<sub>2</sub> uptake is less important in the budget of RO<sub>x</sub> as shown in Fig. 4a, which is in line with the results from Tan et al. (2020).

### 3.5.4 Discussion of uncertainties of $\gamma_{\text{HO}_2}$ estimated in the Wangdu field campaign

The impact of HO<sub>2</sub> aerosol uptake on the RO<sub>x</sub> budget is complicated by large uncertainties in the HO<sub>2</sub> uptake coefficient under ambient conditions. The NEq. is applicable under the assumption of steady-state concentrations and with metastable or liquid aerosol particles (if the ambient RH over a completely liquid aerosol decreases below the deliquescence RH, the aerosol may not crystallize immediately but may constitute a supersaturated aqueous solution (i.e., in the metastable state) (Song et al., 2018)). The approximate calculation of HO<sub>2</sub> concentration gradients within the aerosol particle condensed phase also cause deviations for larger particles or high copper equivalent concentration.

Organic content of an aerosol particle may affect several important parameters in the uptake model (Lakey et al., 2016b, 2015). 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 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 matter would change the value of  $\gamma_{\text{HO}_2}$ . We tested the core-shell morphology of aerosol particles' influence on HO<sub>2</sub> uptake in the Wangdu campaign (details in the Supplement). Organic matter will lower the uptake coefficient about 25 % to 40 % under the assumption that 20 %–50 % PM<sub>2.5</sub> mass is organic matter.

Another uncertainty comes from aerosol particles' morphology. The bulk diffusion coefficient of HO<sub>2</sub> and other reactive molecules should be lower in the situation of semi-solid particles (Berkemeier et al., 2016; Shiraiwa et al., 2010;

Mikhailov et al., 2009) and would change with the water activity and the organic components (Price et al., 2015). For crystalline or amorphous solid aerosol particles, HO<sub>2</sub> 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  $\gamma_{\text{HO}_2}$  with semi-solid aerosol particles. In the Wangdu campaign,  $\kappa_{\text{sca}}$  (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 does not significantly influence  $\gamma_{\text{HO}_2}$ . In any case, aerosol particles' morphology relative to an aqueous phase will influence the uptake coefficient of HO<sub>2</sub>. The uptake process would vary with mixing state of the particles; thus the predicted  $\gamma_{\text{HO}_2}$  values here may be biased as a result but represent an average over bulk aerosols.

The interaction between organics and soluble copper and the influence of organics on aerosol properties will lead to further uncertainty in the calculation of the uptake coefficient. Lakey et al. (2016a, b, 2015) also showed that the addition of an organic compound to Cu<sup>2+</sup>-doped aerosols such as oxalic acid, which forms oxalate ions (C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup> in the aerosol, results in a lower value of  $\gamma_{\text{HO}_2}$  as such ions form a complex with the TMIs.

As noted above, the value ( $0.116 \pm 0.086$  ( $1\sigma$ )) estimated by the NEq. represents the upper limitation of  $\gamma_{\text{HO}_2}$  in the Wangdu field campaign.

#### 4 Summary and conclusions

Taketani et al. (2012) collected the filter samples of aerosol in Mt. Tai and Mt. Mang, North China, 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. (2019b) suggest that the rapid decrease of PM<sub>2.5</sub> in China has slowed down the reactive uptake rate of HO<sub>2</sub> radicals by aerosol particles and could have been the main reason for the increase in ozone in the North China Plain in recent years. They apply a value of the uptake coefficient of 0.2 in their model calculations. However, the results of the MARK model and of the NEq. in this paper suggest that the HO<sub>2</sub> 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 the heterogeneous uptake of HO<sub>2</sub> in the gas phase and heterogeneous physicochemical reactions under different environmental conditions in different regions. The novel parameterized equation proposed in this paper provides an effective way for a more detailed calculation of the effects of HO<sub>2</sub> heterogeneous reactions on the atmospheric radical budget, ozone production, and particu-

late matter generation. This is the first attempt to parameterize the heterogeneous uptake coefficient of HO<sub>2</sub> with aerosol particles in a campaign in China. This equation estimates the  $\gamma_{\text{HO}_2}$  in a comprehensive field campaign, which is in agreement with the simulation results from the comparison of gas-phase radical concentrations (Tan et al., 2020). Overall, we can conclude that the HO<sub>2</sub> uptake process needs to be considered in photochemical box models for the study of the HO<sub>x</sub> 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 and organic content, as well as the aerosol liquid water, should be included in future field campaigns for the study of the HO<sub>x</sub> radical budget.

## Appendix A

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

| Parameter                                                                         | Description                                                                                                                                                                                                                                                                               | Unit                                                  |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------|
| Used in the parameterized equation                                                |                                                                                                                                                                                                                                                                                           |                                                       |
| $\gamma_{\text{HO}_2}$                                                            | HO <sub>2</sub> uptake coefficient                                                                                                                                                                                                                                                        | –                                                     |
| $\alpha_{\text{HO}_2}$                                                            | Mass accommodation coefficient of HO <sub>2</sub> which is the probability that a HO <sub>2</sub> molecule colliding with the aerosol surface leads to dissolution, reaction, or volatilization                                                                                           | –                                                     |
| $v_{\text{HO}_2}$                                                                 | Mean molecular speed of HO <sub>2</sub>                                                                                                                                                                                                                                                   | cm s <sup>−1</sup>                                    |
| $R_d$                                                                             | Count median diameter of the aerosol particles                                                                                                                                                                                                                                            | cm                                                    |
| $R_c$                                                                             | Radius of the aqueous core                                                                                                                                                                                                                                                                | cm                                                    |
| $H_{\text{corr}}$                                                                 | Henry's constant corrected for solution pH $H_{\text{corr}} = H_0 \times \left(1 + \frac{K_{\text{eq}}}{[H^+]}\right)$                                                                                                                                                                    | mol cm <sup>−3</sup> atm <sup>−1</sup>                |
| $H_0$                                                                             | Physical Henry's law constant                                                                                                                                                                                                                                                             | mol cm <sup>−3</sup> atm <sup>−1</sup>                |
| $H^{\text{cc}}$                                                                   | Effective Henry's law constant                                                                                                                                                                                                                                                            | mol cm <sup>−3</sup> atm <sup>−1</sup>                |
| $H_{\text{org}}$                                                                  | Henry's law constant of HO <sub>2</sub> for organic coating                                                                                                                                                                                                                               | mol cm <sup>−3</sup> atm <sup>−1</sup>                |
| $R$                                                                               | Gas constant                                                                                                                                                                                                                                                                              | cm <sup>3</sup> atm K <sup>−1</sup> mol <sup>−1</sup> |
| $T$                                                                               | Temperature                                                                                                                                                                                                                                                                               | K                                                     |
| RH                                                                                | Relative humidity ranging from 0.4 to 0.9                                                                                                                                                                                                                                                 | 0–1                                                   |
| ALWC                                                                              | Aerosol liquid water content                                                                                                                                                                                                                                                              | g cm <sup>−3</sup>                                    |
| [PM]                                                                              | Mass concentration of PM <sub>2.5</sub>                                                                                                                                                                                                                                                   | μg cm <sup>−3</sup>                                   |
| $D_g$                                                                             | Gas-phase diffusion coefficient of HO <sub>2</sub>                                                                                                                                                                                                                                        | cm <sup>2</sup> s <sup>−1</sup>                       |
| $D_{\text{aq}}$                                                                   | Aqueous-phase diffusion coefficient                                                                                                                                                                                                                                                       | cm <sup>2</sup> s <sup>−1</sup>                       |
| $D_{\text{org}}$                                                                  | Solubility and diffusivity of HO <sub>2</sub> in the organic coating                                                                                                                                                                                                                      | cm <sup>2</sup> s <sup>−1</sup>                       |
| $\varepsilon$                                                                     | Ratio of the radius of the aqueous core ( $R_c$ ) and the particle ( $R_d$ ).                                                                                                                                                                                                             | –                                                     |
| $l$                                                                               | Thickness of organic coating which is calculated from the volume ratio of the inorganics to the total particle volume with the assumption of a hydrophobic organic coating (density, 1.27 g cm <sup>−3</sup> ) on the aqueous inorganic core (with a density of 1.77 g cm <sup>−3</sup> ) | cm                                                    |
| Used in the corrections in the MARK model or the classical parameterized equation |                                                                                                                                                                                                                                                                                           |                                                       |
| $\rho$                                                                            | Density of the aerosol particles                                                                                                                                                                                                                                                          | g cm <sup>−3</sup>                                    |
| $I$                                                                               | Solution molar ionic strength                                                                                                                                                                                                                                                             | M                                                     |
| $A$                                                                               | Activity coefficient for gas-phase HO <sub>2</sub> and other neutral small molecules                                                                                                                                                                                                      | –                                                     |
| $\varphi_x$                                                                       | Activity coefficient of ion in solution                                                                                                                                                                                                                                                   | –                                                     |
| $m_y$                                                                             | Molality of an ion in solution                                                                                                                                                                                                                                                            | M                                                     |
| $\varepsilon(xyI)$                                                                | Interaction coefficients; the summation extends over all ions ( $y$ ) in the solution at a molality of $m_y$                                                                                                                                                                              | –                                                     |
| $[x_i]_{\text{eff}}$                                                              | Effective molality of an ion $x_i$                                                                                                                                                                                                                                                        | M                                                     |
| $[\text{HO}_2]$                                                                   | Averaged steady-state HO <sub>2</sub> concentration over the volume of the particle                                                                                                                                                                                                       | M                                                     |
| $[\text{HO}_{2(r)}]$                                                              | HO <sub>2</sub> concentration at the surface of particles                                                                                                                                                                                                                                 | M                                                     |
| $K_{\text{eq}}$                                                                   | Solution equilibrium constant for HO <sub>2</sub> in the gas phase                                                                                                                                                                                                                        | M <sup>−1</sup> s <sup>−1</sup>                       |
| $k_{\text{eff}}$                                                                  | Comprehensive liquid-phase reaction rate coefficient which encompasses both HO <sub>2</sub> dissolution equilibrium reactions and liquid-phase chemical–physical reactions during HO <sub>2</sub> uptake process                                                                          | M <sup>−1</sup> s <sup>−1</sup>                       |
| $k_{\text{TMI}}$                                                                  | Second-order rate coefficient ( $k_{\text{TMI}}$ ) of HO <sub>2</sub> and O <sub>2</sub> <sup>−</sup> with transition metal ions used in the classical equation                                                                                                                           | M <sup>−1</sup> s <sup>−1</sup>                       |
| $k^1$                                                                             | Effective rate coefficient used in the classical equation proposed by IUPAC                                                                                                                                                                                                               | M <sup>−1</sup> s <sup>−1</sup>                       |

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

**Supplement.** The supplement related to this article is available online at: <https://doi.org/10.5194/acp-20-15835-2020-supplement>.

**Author contributions.** KL conceived the study. HS and KL developed the MARK model for multiphase simulations. XC and QZ improved the codes of the MARK model. ZT, HF, KL, AW, MZ, AW, AKS, and YZ contributed to the related measurements of the Wangdu field campaign. DEH, DRM, and MTBR contributed the laboratory studies of HO<sub>2</sub> uptake coefficients, and they contributed to the writing of the manuscript. HS performed the model simulations and prepared the manuscript with KL and ZT, which was enhanced by contributions from all the co-authors.

**Competing interests.** The authors declare that they have no conflict of interest.

**Acknowledgements.** We gratefully acknowledge the kind help from Lisa Whalley for her technical help of the HO<sub>2</sub> uptake measurement and the science team of the Wangdu field campaign.

**Financial support.** This research has been supported by the Beijing Municipal Natural Science Foundation for Distinguished Young Scholars (grant no. JQ19031), the National Natural Science Foundation of China (grant nos. 21976006, 91544225, 21522701, and 91844301), and the National Research Program for Key Issues in Air Pollution Control (grant no. DQGG0103-01).

**Review statement.** This paper was edited by Markus Ammann and reviewed by four anonymous referees.

## References

- Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, *Atmos. Chem. Phys.*, 13, 8045–8228, <https://doi.org/10.5194/acp-13-8045-2013>, 2013.
- Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Pöschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy, semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, *Phys. Chem. Chem. Phys.*, 18, 12662–12674, 2016.
- Bian, Y. X., Zhao, C. S., Ma, N., Chen, J., and Xu, W. Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, *Atmos. Chem. Phys.*, 14, 6417–6426, <https://doi.org/10.5194/acp-14-6417-2014>, 2014.
- 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.
- Capps, S. L., Henze, D. K., Hakami, A., Russell, A. G., and Nenes, A.: ANISORROPIA: the adjoint of the aerosol thermodynamic model ISORROPIA, *Atmos. Chem. Phys.*, 12, 527–543, <https://doi.org/10.5194/acp-12-527-2012>, 2012.
- Chameides, W. L. and Stelson, A. W.: Aqueous-phase chemical processes in deliquescent seasalt aerosols, *Ber. Bunsen Phys. Chem.*, 96, 461–470, 1992.
- Cheng, M. C., You, C. F., Cao, J. J., and Jin, Z. D.: Spatial and seasonal variability of water-soluble ions in PM<sub>2.5</sub> aerosols in 14 major cities in China, *Atmos. Environ.*, 60, 182–192, <https://doi.org/10.1016/j.atmosenv.2012.06.037>, 2012.
- Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H<sup>+</sup>–NH<sub>4</sub><sup>+</sup>–SO<sub>4</sub><sup>2−</sup>–NO<sub>3</sub><sup>−</sup>–H<sub>2</sub>O at tropospheric temperatures, *J. Phys. Chem. A*, 102, 2137–2154, <https://doi.org/10.1021/jp973042r>, 1998.
- Cooper, P. L. and Abbatt, J. P. D.: Heterogeneous interactions of OH and HO<sub>2</sub> radicals with surfaces characteristic of atmospheric particulate matter, *J. Phys. Chem.-Us.*, 100, 2249–2254, <https://doi.org/10.1021/Jp952142z>, 1996.
- 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, <https://doi.org/10.5194/acp-19-7939-2019>, 2019.
- Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, *Environ. Sci. Technol.*, 51, 2611–2620, <https://doi.org/10.1021/acs.est.6b06151>, 2017.
- Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K<sup>+</sup>–Ca<sup>2+</sup>–Mg<sup>2+</sup>–NH<sub>4</sub><sup>+</sup>–Na<sup>+</sup>–SO<sub>4</sub><sup>2−</sup>–NO<sub>3</sub><sup>−</sup>–Cl<sup>−</sup>–H<sub>2</sub>O aerosols, *Atmos. Chem. Phys.*, 7, 4639–4659, <https://doi.org/10.5194/acp-7-4639-2007>, 2007.
- 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 sub-micron inorganic salt aerosols, *Phys. Chem. Chem. Phys.*, 15, 12829–12845, 2013.
- Golden, D. M., Bierbaum, V. M., and Howard, C. J.: Re-evaluation of the bond-dissociation energies (Delta-Hd<sub>be</sub>) for H-OH, H-OOH, H-OO-, H-O-, H-OO-, and H-OO, *J. Phys. Chem.-Us.*, 94, 5413–5415, <https://doi.org/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, <https://doi.org/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, <https://doi.org/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, <https://doi.org/10.1029/93jd02932>, 1994.
- Heard, D. E. and Pilling, M. J.: Measurement of OH and HO<sub>2</sub> in the troposphere, *Chem. Rev.*, 103, 5163–5198, <https://doi.org/10.1021/cr020522s>, 2003.

- Hsu, S.-C., Liu, S. C., Lin, C. Y., Hsu, R. T., Huang, Y. T., and Chen, Y. W.: Metal compositions of PM<sub>10</sub> and PM<sub>2.5</sub> aerosols in Taipei during spring, 2002, *Terr. Atmos. Ocean. Sci.*, 15, 925–948, [https://doi.org/10.3319/tao.2004.15.5.925\(adse\)](https://doi.org/10.3319/tao.2004.15.5.925(adse)), 2004.
- Hsu, S.-C., Wong, G. T. F., Gong, G.-C., Shiah, F.-K., Huang, Y.-T., Kao, S.-J., Tsai, F., Candice Lung, S.-C., Lin, F.-J., Lin, I. I., Hung, C.-C., and Tseng, C.-M.: Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea, *Mar. Chem.*, 120, 116–127, <https://doi.org/10.1016/j.marchem.2008.10.003>, 2010a.
- Hsu, S.-C., Liu, S. C., Tsai, F., Engling, G., Lin, I., Chou, C. K. C., Kao, S. J., Lung, S. C. C., Chan, C. Y., Lin, S. C., Huang, J. C., Chi, K. H., Chen, W. N., Lin, F. J., Huang, C. H., Kuo, C. L., Wu, T. C., and Huang, Y. T.: High wintertime particulate matter pollution over an offshore island (Kinmen) off southeastern China: An overview, *J. Geophys. Res.-Atmos.*, 115, <https://doi.org/10.1029/2009jd013641>, 2010b.
- Hu, J., Shi, Q., Davidovits, P., Worsnop, D., Zahniser, M., and Kolb, C.: Reactive uptake of Cl<sub>2(g)</sub> and Br<sub>2(g)</sub> by aqueous surfaces as a function of Br<sup>−</sup> and I<sup>−</sup> ion concentration: The effect of chemical reaction at the interface, *J. Phys. Chem.*, 99, 8768–8776, 1995.
- Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 34, 2131–2159, [https://doi.org/10.1016/s1352-2310\(99\)00462-8](https://doi.org/10.1016/s1352-2310(99)00462-8), 2000.
- Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Tanimoto, H., Kato, S., Suthawaree, J., Inomata, S., Taketani, F., Okuzawa, K., Kawamura, K., Akimoto, H., and Wang, Z. F.: Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors, *Atmos. Chem. Phys.*, 9, 7711–7723, <https://doi.org/10.5194/acp-9-7711-2009>, 2009.
- 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 Sci., 3, 771–875, 1995.
- Kuang, Y., Zhao, C. S., Zhao, G., Tao, J. C., Xu, W., Ma, N., and Bian, Y. X.: A novel method for calculating ambient aerosol liquid water content based on measurements of a humidified nephelometer system, *Atmos. Meas. Tech.*, 11, 2967–2982, <https://doi.org/10.5194/amt-11-2967-2018>, 2018.
- Kuang, Y., Tao, J., Xu, W., Yu, Y., Zhao, G., Shen, C., Bian, Y., and Zhao, C.: Calculating ambient aerosol surface area concentrations using aerosol light scattering enhancement measurements, *Atmos. Environ.*, 216, 116919, <https://doi.org/10.1016/j.atmosenv.2019.116919>, 2019.
- Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO<sub>2</sub> Uptake Coefficients onto Single Component Organic Aerosols, *Environ. Sci. Technol.*, 49, 4878–4885, <https://doi.org/10.1021/acs.est.5b00948>, 2015.
- Lakey, P. S. J., Berkemeier, T., Krapf, M., Dommen, J., Steimer, S. S., Whalley, L. K., Ingham, T., Baeza-Romero, M. T., Pöschl, U., Shiraiwa, M., Ammann, M., and Heard, D. E.: The effect of viscosity and diffusion on the HO<sub>2</sub> uptake by sucrose and secondary organic aerosol particles, *Atmos. Chem. Phys.*, 16, 13035–13047, <https://doi.org/10.5194/acp-16-13035-2016>, 2016a.
- 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, *J. Phys. Chem. A*, 120, 1421–1430, <https://doi.org/10.1021/acs.jpca.5b06316>, 2016b.
- Lelieveld, J. and Crutzen, P. J.: The role of clouds in tropospheric photochemistry, *J. Atmos. Chem.*, 12, 229–267, <https://doi.org/10.1007/bf00048075>, 1991.
- Lewis, J., Argyle, R., Bunclark, P., Evans, D., Gonzales-Solares, E., and Markwardt, C. B.: Non-linear Least Squares Fitting in IDL with MPFIT, arXiv preprint arXiv:0902.2850, 2009.
- Li, H., Wang, D., Cui, L., Gao, Y., Huo, J., Wang, X., Zhang, Z., Tan, Y., Huang, Y., Cao, J., Chow, J. C., Lee, S.-c., and Fu, Q.: Characteristics of atmospheric PM<sub>2.5</sub> composition during the implementation of stringent pollution control measures in Shanghai for the 2016 G20 summit, *Sci. Total Environ.*, 648, 1121–1129, <https://doi.org/10.1016/j.scitotenv.2018.08.219>, 2019a.
- Li, K., Jacob, D. J., Liao, H., Shen, L., Zhang, Q., and Bates, K. H.: Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, *P. Natl. Acad. Sci. USA*, 116, 422, <https://doi.org/10.1073/pnas.1812168116>, 2019b.
- Lou, S., Liao, H., and Zhu, B.: Impacts of aerosols on surface-layer ozone concentrations in China through heterogeneous reactions and changes in photolysis rates, *Atmos. Environ.*, 85, 123–138, <https://doi.org/10.1016/j.atmosenv.2013.12.004>, 2014.
- Macintyre, H. L. and Evans, M. J.: Parameterisation and impact of aerosol uptake of HO<sub>2</sub> on a global tropospheric model, *Atmos. Chem. Phys.*, 11, 10965–10974, <https://doi.org/10.5194/acp-11-10965-2011>, 2011.
- Magi, L., Schweitzer, F., Pallares, C., Cherif, S., Mirabel, P., and George, C.: Investigation of the uptake rate of ozone and methyl hydroperoxide by water surfaces, *J. Phys. Chem. A*, 101, 4943–4949, 1997.
- Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. St., Crounse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HO<sub>x</sub>) in the Arctic troposphere in spring, *Atmos. Chem. Phys.*, 10, 5823–5838, <https://doi.org/10.5194/acp-10-5823-2010>, 2010.
- Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, *Atmos. Chem. Phys.*, 13, 509–519, <https://doi.org/10.5194/acp-13-509-2013>, 2013.
- Markwardt, C. B.: Non-linear least squares fitting in IDL with MPFIT, arXiv preprint arXiv:0902.2850, 2009.
- Martin, R. V., Jacob, D. J., Yantosca, R. M., Chin, M., and Ginoux, P.: Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, *J. Geophys. Res.-Atmos.*, 108, 4097, <https://doi.org/10.1029/2002jd002622>, 2003.
- Martinez, M., Harder, H., Kovacs, T. A., Simpας, J. B., Bassis, J., Leshner, R., Brune, W. H., Frost, G. J., Williams, E. J., Stroud, C. A., Jobson, B. T., Roberts, J. M., Hall, S. R., Shetter, R. E., Wert, B., Fried, A., Alicke, B., Stutz, J., Young, V. L., White, A. B., and Zamora, R. J.: OH and HO<sub>2</sub> concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999, *J. Geophys. Res.-Atmos.*, 108, 4617, <https://doi.org/10.1029/2003jd003551>, 2003.

- Matthews, P. S. J., Baeza-Romero, M. T., Whalley, L. K., and Heard, D. E.: Uptake of HO<sub>2</sub> radicals onto Arizona test dust particles using an aerosol flow tube, *Atmos. Chem. Phys.*, 14, 7397–7408, <https://doi.org/10.5194/acp-14-7397-2014>, 2014.
- Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, *Atmos. Chem. Phys.*, 9, 9491–9522, <https://doi.org/10.5194/acp-9-9491-2009>, 2009.
- Moon, D. R., Taverna, G. S., Anduix-Canto, C., Ingham, T., Chipperfield, M. P., Seakins, P. W., Baeza-Romero, M.-T., and Heard, D. E.: Heterogeneous reaction of HO<sub>2</sub> with airborne TiO<sub>2</sub> particles and its implication for climate change mitigation strategies, *Atmos. Chem. Phys.*, 18, 327–338, <https://doi.org/10.5194/acp-18-327-2018>, 2018.
- Mozurkewich, M., Mcmurry, P. H., Gupta, A., and Calvert, J. G.: Mass Accommodation Coefficient for HO<sub>2</sub> Radicals on Aqueous Particles, *J. Geophys. Res.-Atmos.*, 92, 4163–4170, 1987.
- Müller, B. and Heal, M. R.: The mass accommodation coefficient of ozone on an aqueous surface, *Phys. Chem. Chem. Phys.*, 4, 3365–3369, 2002.
- Price, H. C., Mattsson, J., Zhang, Y., Bertram, A. K., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., and Rickards, A. M.: Water diffusion in atmospherically relevant  $\alpha$ -pinene secondary organic material, *Chem. Sci.*, 6, 4876–4883, 2015.
- Ross, H. B. and Noone, K. J.: A numerical investigation of the destruction of peroxy radical by Cu ion catalyzed-reactions of atmospheric particles, *J. Atmos. Chem.*, 12, 121–136, <https://doi.org/10.1007/bf00115775>, 1991.
- Sander, R.: Modeling atmospheric chemistry: Interactions between gas-phase species and liquid cloud/aerosol particles, *Surv. Geophys.*, 20, 1–31, 1999.
- Schwartz, S. E. and Freiberg, J. E.: Mass-transport limitation of the rate of reaction of gases in liquid droplets-application to oxidation of SO<sub>2</sub> in aqueous solutions, *Atmos. Environ.*, 15, 1129–1144, [https://doi.org/10.1016/0004-6981\(81\)90303-6](https://doi.org/10.1016/0004-6981(81)90303-6), 1981.
- 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, <https://doi.org/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.
- Schwartz, S. E.: Both sides now-The chemistry of clouds, *Annals of the New York Academy of Sciences*, 502, 83–144, <https://doi.org/10.1111/j.1749-6632.1987.tb37648.x>, 1987.
- Seinfeld, J. H.: ES&T books: atmospheric chemistry and physics of air pollution, *Environ. Sci. Technol.*, 20, 863–863, 1986.
- Shiraiwa, M., Pfrang, C., and Pöschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, *Atmos. Chem. Phys.*, 10, 3673–3691, <https://doi.org/10.5194/acp-10-3673-2010>, 2010.
- Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, *Atmos. Chem. Phys.*, 18, 7423–7438, <https://doi.org/10.5194/acp-18-7423-2018>, 2018.
- 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, *J. Phys. Chem. 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.
- Taketani, F. and Kanaya, Y.: Kinetics of HO<sub>2</sub> Uptake in Levoglucosan and Polystyrene Latex Particles, *J. Phys. Chem. Lett.*, 1, 1701–1704, <https://doi.org/10.1021/jz100478s>, 2010.
- Taketani, F., Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Okuzawa, K., Kawamura, K., Wang, Z., and Akimoto, H.: Measurement of overall uptake coefficients for HO<sub>2</sub> radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang (China), *Atmos. Chem. Phys.*, 12, 11907–11916, <https://doi.org/10.5194/acp-12-11907-2012>, 2012.
- Tan, Z., Hofzumahaus, A., Lu, K., Brown, S. S., Holland, F., Huey, L. G., Kiendler-Scharr, A., Li, X., Liu, X., and Ma, N.: No Evidence for a Significant Impact of Heterogeneous Chemistry on Radical Concentrations in the North China Plain in Summer 2014, *Environ. Sci. Technol.*, 54, 5973–5979, <https://doi.org/10.1021/acs.est.0c00525>, 2020.
- Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häsel, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals, *Atmos. Chem. Phys.*, 17, 663–690, <https://doi.org/10.5194/acp-17-663-2017>, 2017.
- Tang, M., Huang, X., Lu, K., Ge, M., Li, Y., Cheng, P., Zhu, T., Ding, A., Zhang, Y., Gligorovski, S., Song, W., Ding, X., Bi, X., and Wang, X.: Heterogeneous reactions of mineral dust aerosol: implications for tropospheric oxidation capacity, *Atmos. Chem. Phys.*, 17, 11727–11777, <https://doi.org/10.5194/acp-17-11727-2017>, 2017.
- 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, 9485–9518, <https://doi.org/10.5194/acp-17-9485-2017>, 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, <https://doi.org/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, *J. Geophys. Res.-Atmos.*, 113, D05303, <https://doi.org/10.1029/2007JD0092361>, 2008.
- Tie, X., Brasseur, G., Emmons, L., Horowitz, L., and Kinnison, D.: Effects of aerosols on tropospheric oxidants: A global model study, *J. Geophys. Res.-Atmos.*, 106, 22931–22964, <https://doi.org/10.1029/2001jd900206>, 2001.
- Utter, R. G., Burkholder, J. B., Howard, C. J., and Ravishankara, A. R.: Measurement of the mass accommodation coefficient of ozone on aqueous surfaces, *J. Phys. Chem.-Us.*, 96, 4973–4979, <https://doi.org/10.1021/j100191a045>, 1992.



- Whalley, L. K., Furneaux, K. L., Goddard, A., Lee, J. D., Mahajan, A., Oetjen, H., Read, K. A., Kaaden, N., Carpenter, L. J., Lewis, A. C., Plane, J. M. C., Saltzman, E. S., Wiedensohler, A., and Heard, D. E.: The chemistry of OH and HO<sub>2</sub> radicals in the boundary layer over the tropical Atlantic Ocean, *Atmos. Chem. Phys.*, 10, 1555–1576, <https://doi.org/10.5194/acp-10-1555-2010>, 2010.
- Whalley, L. K., Stone, D., George, I. J., Mertes, S., van Pinxteren, D., Tilgner, A., Herrmann, H., Evans, M. J., and Heard, D. E.: The influence of clouds on radical concentrations: observations and modelling studies of HO<sub>x</sub> during the Hill Cap Cloud Thuringia (HCCT) campaign in 2010, *Atmos. Chem. Phys.*, 15, 3289–3301, <https://doi.org/10.5194/acp-15-3289-2015>, 2015.
- Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, *Atmos. Chem. Phys.*, 14, 13175–13188, <https://doi.org/10.5194/acp-14-13175-2014>, 2014.
- Yin, J., Allen, A. G., Harrison, R. M., Jennings, S. G., Wright, E., Fitzpatrick, M., Healy, T., Barry, E., Ceburnis, D., and McCusker, D.: Major component composition of urban PM<sub>10</sub> and PM<sub>2.5</sub> in Ireland, *Atmos. Res.*, 78, 149–165, <https://doi.org/10.1016/j.atmosres.2005.03.006>, 2005.
- 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 Chem. Lett.*, 30, 2236–2240, <https://doi.org/10.1016/j.cclet.2019.07.041>, 2019.