



Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols

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Abstract. The hydroperoxyl radical (HO_2) is a major precursor of OH and tropospheric ozone. OH is the main atmospheric oxidant, while tropospheric ozone is an important surface pollutant and greenhouse gas. Standard gas-phase models for atmospheric chemistry tend to overestimate observed HO_2 concentrations, and this has been tentatively attributed to heterogeneous uptake by aerosol particles. It is generally assumed that HO_2 uptake by aerosol involves conversion to H_2O_2 , but this is of limited efficacy as an HO_2 sink because H_2O_2 can photolyze to regenerate OH and from there HO_2 . Joint atmospheric observations of HO_2 and H_2O_2 suggest that HO_2 uptake by aerosols may in fact not produce H_2O_2 . Here we propose a catalytic mechanism involving coupling of the transition metal ions Cu(I)/Cu(II) and Fe(II)/Fe(III) to rapidly convert HO_2 to H_2O in aqueous aerosols. The implied HO_2 uptake and conversion to H_2O significantly affects global model predictions of tropospheric OH, ozone, carbon monoxide (CO) and other species, improving comparisons to observations in the GEOS-Chem model. It represents a previously unrecognized positive radiative forcing of aerosols through the effects on the chemical budgets of major greenhouse gases including methane and hydrofluorocarbons (HFCs).

1 Introduction

HO_2 in the troposphere cycles rapidly with other members of the hydrogen oxide radical family ($\text{HO}_x \equiv \text{OH} + \text{H} + \text{HO}_2$ + organic peroxy and oxy radicals). This cycling determines OH levels and ozone

production. The main sources of HO_x are photolysis of ozone in the presence of water vapor and photolysis of carbonyls. The sinks involve formation of peroxides, HNO_3 , and water. Peroxides and HNO_3 can photolyze, returning HO_x . Formation of water is a terminal sink. HO_2 is in general the dominant component of HO_x , so that the budget of HO_2 is largely defined by that of HO_x .

Uptake of HO_2 by aqueous aerosols is promoted by its high solubility in water (Henry's law constant $2.0 \times 10^3 \text{ M atm}^{-1}$ at 298 K) and aqueous-phase dissociation to O_2^- ($\text{pK}_a = 4.7$), with rapid ensuing ionic redox chemistry. The efficacy of uptake is commonly measured by the reactive uptake coefficient, $\gamma(\text{HO}_2)$, defined as the fraction of HO_2 collisions with aerosol surfaces resulting in reaction. Direct reaction of $\text{HO}_2(\text{aq})$ with O_2^- produces H_2O_2 but the corresponding $\gamma(\text{HO}_2)$ is relatively low, ranging from 0.01 for acidic aerosols (Thornton and Abbatt, 2005) to 0.2 for neutralized aerosols (Thornton and Abbatt, 2005; Taketani et al., 2008). Higher values of $\gamma(\text{HO}_2)$, approaching unity, have been measured for Cu-doped aerosols where Cu(I)/Cu(II) redox cycling catalyzes $\text{HO}_2^-/\text{O}_2^-$ conversion to H_2O_2 (Mozurkewich et al., 1987; Cooper and Abbatt, 1996; Thornton and Abbatt, 2005; Taketani et al., 2008). Model calculations suggest that other aerosol transition metal ions (TMI), including Fe(II)/Fe(III) and Mn(II)/Mn(III), can drive similar chemistry (Graedel et al., 1986). Uptake of HO_2 by non-aqueous inorganic aerosol appears to be very slow (Cooper and Abbatt, 1996; Taketani et al., 2008), but can be significant for carbonaceous aerosols (up to 0.13 for levoglucosan particles) (Bedjanian et al., 2005; Taketani et al., 2010).

Table 1. Field evidence for HO₂ aerosol uptake^a.

Location	Type	HO ₂ Conc (pptv) ^b	Estimated γ (HO ₂)	Comments	Reference
Mauna Loa, Hawaii	remote	15 ^c	0.5–1		Cantrell et al. (1996)
Southern Ontario, Canada	rural	10	~1	To reduce HO _x by more than a factor of 2	Plummer et al. (1996)
Oki Island, Japan	remote	10	~1	To reduce HO ₂ by 50 %	Kanaya et al. (2000)
TRACE-P aircraft campaign	plume in free troposphere		N/A	30 %–50 % loss of peroxy radicals onto aerosols	Cantrell et al. (2003a)
TOPSE aircraft campaign	remote	5	N/A		Cantrell et al. (2003b)
Remote marine boundary layer near Australia	remote	8	1		Sommariva et al. (2004); Haggerstone et al. (2005)
Saharan dust plume	plume	15 ^c	1	No H ₂ O ₂ formed from HO ₂ uptake. Also needs uptake for H ₂ O ₂ .	de Reus et al. (2005)
Mace Head, Ireland	remote	6	1		Sommariva et al. (2006)
Rishiri Island, Japan	remote	6	1		Kanaya et al. (2007)
Jungfraujoch research station ^d	remote	6	1		Parker et al. (2009)
Biomass burning plumes in West Africa	plume		N/A	Modeled HO ₂ is higher than measured HO ₂ by a factor of 5.	Commane et al. (2010)
Arctic spring	remote	5	~1		Mao et al. (2010a); Olson et al. (2012)
Arctic summer	remote	10	~1		Olson et al. (2012)

^a γ (HO₂) for all aerosol inferred from photochemical modeling of observed HO₂ concentrations.

^b noontime mean or median value

^c estimated from the measured total peroxy radicals (HO₂ + RO₂).

^d estimated for the uptake on snow surface.

Standard gas-phase models for atmospheric chemistry tend to overestimate observed HO₂ concentrations, and this has been tentatively attributed to heterogeneous uptake by aerosol particles. As shown in Table 1, HO_x loss by HO₂ uptake is significant where HO_x concentrations are relatively low (HO₂ is typically less than 10 ppt) and/or aerosol loading is high. In contrast, HO_x loss by HO₂ uptake is less apparent where HO₂ concentration is a few tens of ppt such as urban areas (Mao et al., 2010b) and forests (Mao et al., 2012). To a large extent this is because HO_x loss through HO₂ + HO₂ and HO₂ + RO₂ is quadratic on HO_x concentrations.

All the laboratory and model mechanisms for HO₂ uptake by aerosol involve conversion to H₂O₂ (Mozurkewich et al., 1987; Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996; Remorov et al., 2002; Bedjanian et al., 2005; Thornton and Abbatt, 2005; Taketani et al., 2008; Thornton et al., 2008; Loukhovitskaya et al., 2009; Taketani et al., 2009; Macintyre and Evans, 2011), but this is of limited efficacy as an HO₂ sink because H₂O₂ can photolyze to regenerate OH and from there HO₂. Joint atmospheric observations of HO₂ and H₂O₂ suggest that HO₂ uptake by aerosols may in fact not produce H₂O₂ (de Reus et al., 2005; Mao et al., 2010a). Previous proposed mechanisms for the conversion of HO₂ to H₂O, including Br₂⁻ + HO₂ (Matthew et al., 2003), HSO₄⁻ + HO₂ (Cooper and Abbatt, 1996), and the HO₂-H₂SO₄ complex (Miller and Francisco, 2001) are not catalytic and thereby less efficient. Here we propose a cat-

alytic mechanism involving coupling of the transition metal ions (TMI) Cu(I)/Cu(II) and Fe(II)/Fe(III) to rapidly convert HO₂ to H₂O in aerosols (Fig. 1).

2 Cu-Fe-HO_x cycling

Cu and Fe are ubiquitous components of crustal and combustion aerosols. Concentrations in rural air are in the range 3–300 ng m⁻³ for Cu and 55–14 500 ng m⁻³ for Fe (Schroeder et al., 1987). The submicron size fraction generally associated with combustion aerosols accounts for 25–100 % of Cu mass and 15–50 % of Fe mass (Tables S1 and S2 in the Supplement). Joint measurements of Cu and Fe in fine particles (PM_{2.5}) show that the molar Cu/Fe ratio is typically below 0.1 (Table S3, Fig. S3). While Cu tends to fully dissolve at pH < 5 (Deguillaume et al., 2005), the solubility of Fe varies greatly, ranging from less than 1 % in soils to 81 % in oil combustion products (Schroth et al., 2009). Observations indicate that the dissolved Cu to Fe molar ratio (hereinafter “Cu/Fe”) is typically 0.01–0.1 (Table S4 in the Supplement).

Cu-catalyzed HO₂ loss to H₂O₂ in acid aerosols proceeds by Reactions (RA1)–(RA2), with similar reactions involving O₂⁻ for higher-pH conditions:

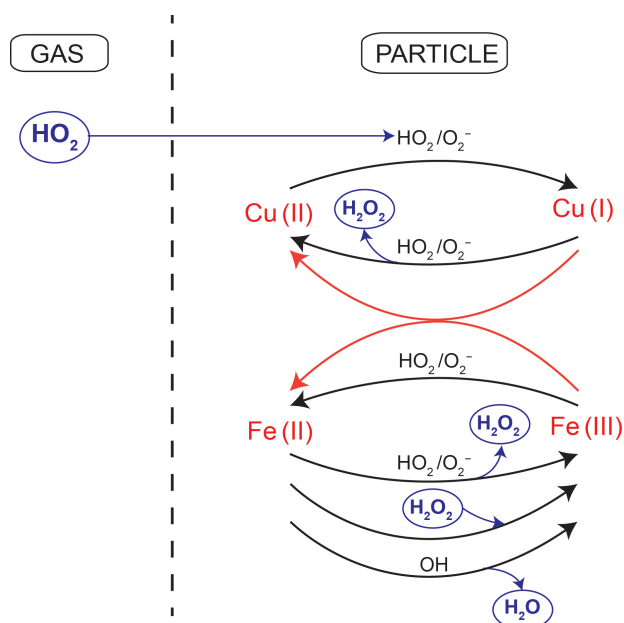
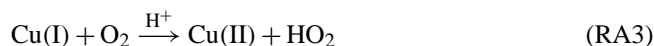
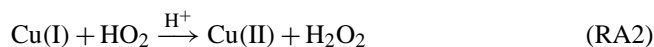
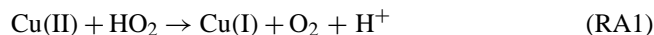


Fig. 1. Cu-Fe redox coupling in aqueous aerosols driven by HO_2 uptake from the gas phase. In the presence of dissolved Cu alone, HO_2 is converted to H_2O_2 . In the presence of both dissolved Cu and Fe, HO_2 is converted to either H_2O_2 or H_2O and may also catalytically consume H_2O_2 .

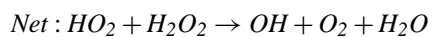
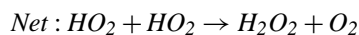
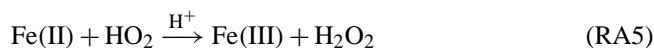


Here the destruction of HO_2 is buffered by the production of HO_2 via (Reaction RA3) (Ervens et al., 2003). Fe-catalyzed HO_2 loss proceeds by a similar cycle though the rate constant of $\text{Fe(III)} + \text{HO}_2$ is two orders of magnitude lower than for Cu(II) (Mozurkewich et al., 1987).

The coupled Cu-Fe catalytic cycle for aqueous-phase HO_2 loss involves (Reaction RA1) and



with three likely pathways for Fe(II) to close the cycle:



The electron transfer reaction $\text{Cu(I)} + \text{Fe(III)}$ (Reaction RA4) is rapid with a rate constant of $1.3\text{--}3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Bjergbakke et al., 1976; Sedlak and

Hoigné, 1993). It has been found previously to regulate the observed diurnal pattern of the Fe(II)/Fe(III) ratio in cloud water (Ervens et al., 2003; Deguillaume et al., 2004). Aerosol chemistry models suggest that (Reaction RA1) is the dominant sink for Cu(II) (Jacob et al., 1989), and we show below that (Reaction RA4) is then the dominant sink for Cu(I) over the expected range of Cu/Fe ratios. The implications for HO_x depend on the fate of Fe(II) . (Reaction RA5) converts HO_x to H_2O_2 while (Reaction RA7) converts HO_x to H_2O . (Reaction RA6) also effectively leads to HO_x loss by converting H_2O_2 to H_2O .

3 Formulation of HO_2 reactive uptake by aerosols

We conducted box model simulations of aqueous aerosol chemistry to examine the effect of Cu-Fe- HO_x cycling by (Reaction RA1)-(Reaction RA7) on the HO_x chemical budget. The chemical mechanism mainly draws from Jacob (2000), Chemical Aqueous Phase Radical Mechanism (CAPRAM) 2.4 (Ervens et al., 2003) and Deguillaume et al. (2004), with a number of modifications and updates (Tables S8 and S9 in the Supplement). A few complexes are included to take into account the speciation of Fe and Cu: Fe(OH)^+ , Fe(OH)_2^+ , $\text{Fe(SO}_4)^+$, Fe(OH)^{2+} , and $\text{CuSO}_4(\text{aq})$. Our simulations are for $T = 298 \text{ K}$ as kinetic data are often not available at low temperatures.

Modeling aerosol aqueous chemistry must account for ionic strength corrections. We use the Aerosol Inorganic Model (Clegg et al., 1998), to calculate the ionic strength and activity coefficients for major ions (i.e. NH_4^+ , H^+ , HSO_4^- , SO_4^{2-}) (Table S6). Activity coefficients for trace metal ions and neutral species are calculated based on specific ion interaction theory or estimated following Ross and Noone (1991) (supplemental material, summarized in Table S7). We also account for the salting out effect on Henry's law constants. We assume Henry's law equilibrium for H_2O_2 , O_3 , and O_2 because of their long lifetimes. Gas uptake of OH is small compared to its aqueous production, in part due to its low Henry's law constant (25 M atm^{-1} at 298 K) (Klaning et al., 1985; Hanson et al., 1992), and in part due to its much lower gas phase concentration than that of HO_2 (Mao et al., 2009). We thus calculate $\text{OH}(\text{aq})$ from aqueous-phase steady state in this model. Concentrations of total dissolved Cu and Fe are held fixed throughout the simulation at their initial values.

The HO_2 uptake and volatilization rates R_{in} and R_{out} (molecules $\text{cm}^{-3} \text{ s}^{-1}$) for a monodisperse aqueous aerosol of radius a can be approximated as (Schwartz, 1986):

$$R_{\text{in}} = \left(\frac{a}{D_g} + \frac{4}{v\alpha} \right)^{-1} A n_{\text{HO}_2} \quad (1)$$

and

$$R_{\text{out}} = \left(\frac{a}{D_g} + \frac{4}{v\alpha} \right)^{-1} A \frac{[\text{HO}_2]_{\text{surf}}}{H^*} \quad (2)$$

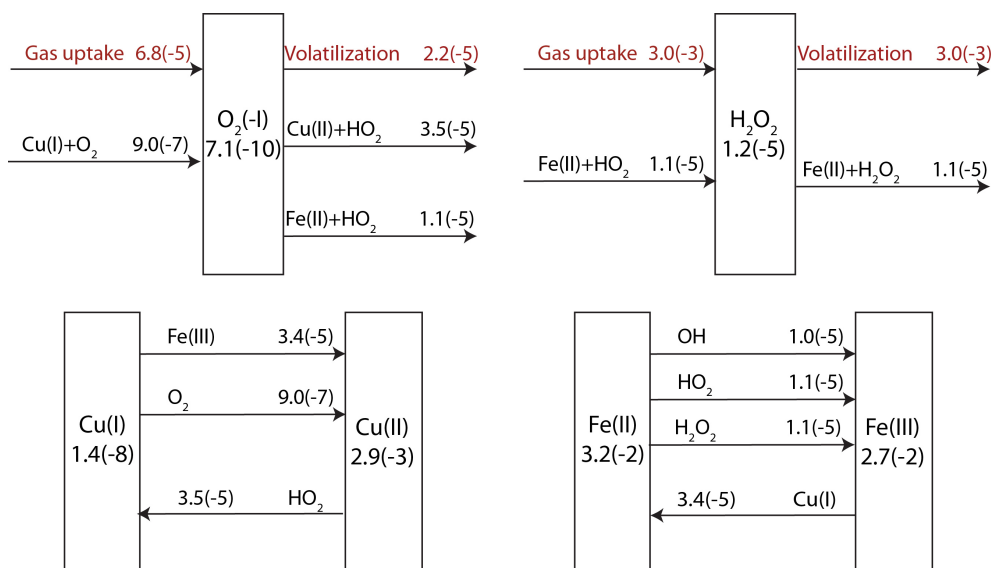


Fig. 2. Simulated aerosol budgets of $\text{O}_2(-\text{I}) \equiv \text{HO}_2(\text{aq}) + \text{O}_2^-$, H_2O_2 , dissolved Cu, and dissolved Fe. The main reaction pathways are indicated. The values shown are aqueous concentrations (M) and transformation rates (M s^{-1}). Read 6.8(-5) as 6.8×10^{-5} . The $\text{Cu(I)} + \text{HO}_2$ reaction (Reaction RA2) is not shown as it is negligibly small under these conditions. Model calculations assume an aqueous NH_4HSO_4 aerosol with dry radius of $0.35 \mu\text{m}$ at $\text{RH} = 85\%$ and $T = 298 \text{ K}$. This simulation is constrained with $\text{HO}_2(\text{g}) = 10 \text{ pptv}$, $\text{H}_2\text{O}_2(\text{g}) = 1 \text{ ppb}$, $\text{O}_3(\text{g}) = 30 \text{ ppb}$. Aerosol pH is 0.15 with ionic strength 7.8 mol kg^{-1} (the resulting activity coefficient $A(\text{Cu}^{2+}) = 0.067$). Dissolved Cu concentration is $2.9 \times 10^{-3} \text{ M}$, adopted from Ross and Noone (1991). The dissolved Cu to Fe molar ratio is $\text{Cu/Fe} = 0.05$.

where n_{HO_2} is the gas phase concentration of HO_2 , A is the aerosol surface area per unit volume of air, v is the mean molecular speed, α is the mass accommodation coefficient assumed here to be unity (Thornton and Abbatt, 2005), D_{g} is the HO_2 gas phase diffusion constant ($0.25 \text{ cm}^2 \text{ s}^{-1}$), $[\text{HO}_2]_{\text{surf}}$ is the concentration at the aerosol surface, and H^* is the effective Henry's law constant corrected for ionic strength and acid dissociation.

The chemical loss rate of aqueous HO_2 is the difference between R_{in} and R_{out} . $\gamma(\text{HO}_2)$ is then defined as the ratio of chemical loss rate to R_{in} . Given the short lifetime of aqueous HO_2 ($\sim 10^{-5} \text{ s}$) against reaction with Cu(II) by (Reaction RA1), the bulk concentration $[\text{HO}_2]_{\text{bulk}}$ and surface concentration $[\text{HO}_2]_{\text{surf}}$ may differ substantially (Schwartz and Freiberg, 1981; Schwartz, 1986). On the basis of the solution to a steady state diffusion equation, their relationship can be expressed as (Jacob, 1986):

$$[\text{HO}_2]_{\text{surf}} = \frac{P_{\text{HO}_2}}{k^I} + ([\text{HO}_2]_{\text{bulk}} - \frac{P_{\text{HO}_2}}{k^I}) \cdot [3(\frac{\coth q}{q} - \frac{1}{q^2})]^{-1} \quad (3)$$

where k^I is the first-order loss constant of HO_2 , P_{HO_2} is the aqueous-phase production rate of HO_2 , and $q = a(\frac{k^I}{D_{\text{aq}}})^{\frac{1}{2}}$ is the diffuso-reactive parameter (Schwartz and Freiberg, 1981), in which D_{aq} is the HO_2 aqueous phase diffusion constant. P_{HO_2} is mainly from (Reaction RA3).

4 Atmospheric model simulations

Figure 2 shows the aqueous-phase chemical budgets of $\text{O}_2(-\text{I}) \equiv \text{HO}_2(\text{aq}) + \text{O}_2^-$, H_2O_2 , Cu, and Fe for a $0.35 \mu\text{m}$ (dry radius) NH_4HSO_4 aerosol at $\text{RH} = 85\%$, with dissolved Cu of $2.9 \times 10^{-3} \text{ M}$ and $\text{Cu/Fe} = 0.05$ (molar). The concentration of Cu is estimated from the measured size distribution of Cu in rural aerosols with total Cu of 3.1 ng m^{-3} (Ross and Noone, 1991). Reactions responsible for less than 1% of total production or loss are not shown. In particular, we find that $\text{Fe(III)} + \text{Cu(I)}$ completely dominates over other pathways for Fe(III) reduction including photolysis and $\text{Fe(III)} + \text{HO}_2$.

In contrast to cloud chemistry (Jacob, 2000), the HO_x budget in aerosols is mainly controlled by TMI chemistry because TMI concentrations are so high. Aqueous OH production and loss are dominated by (Reaction RA6) and (Reaction RA7) respectively. Aqueous HO_2 production within the aerosol accounts for less than 2% of its loss as (Reaction RA4) dominates over (Reaction RA3). The major sinks of aqueous HO_2 are (Reaction RA1) and (Reaction RA5). As shown in Fig. 2, 70% of HO_2 taken up from the gas phase is chemically lost, with the remainder volatilizing. Therefore $\gamma(\text{HO}_2)$ under these conditions is equal to 0.7.

The Cu/Fe ratio is a critical factor in this model calculation. When $\text{Cu/Fe} > 1$, (Reaction RA2) and (Reaction RA3) are the dominant sinks for Cu(I) , leading to the conversion of HO_2 to H_2O_2 . Aerosol pH is also critical. Acid-base dissociation of $\text{HO}_2(\text{aq})/\text{O}_2^-$ at higher pH decreases the HO_2

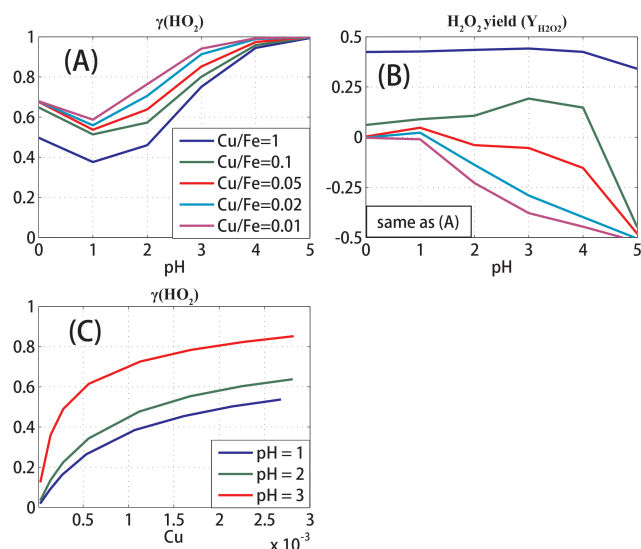


Fig. 3. Impacts of Cu-Fe- HO_x cycling on aerosol chemistry for the model calculations described in the text. (A) and (B): pH dependence of the HO_2 reactive uptake probability $\gamma(\text{HO}_2)$ and the corresponding H_2O_2 yield for a dissolved Cu concentration of 2.9×10^{-3} M and different Cu/Fe molar ratios. (C): dependence of $\gamma(\text{HO}_2)$ on Cu concentrations for different pH values with Cu/Fe = 0.05.

volatilization flux as the reaction rate constants of Cu or Fe with O_2^- can be two orders of magnitude faster than with $\text{HO}_2(\text{aq})$. The speciation of Cu and Fe is affected by pH, and we account for some of the complexation equilibria as described in Sect. 3. Organic complexes may be important for Cu (Thornton et al., 2008) but we have no kinetic data for them. Precipitation of $\text{Fe}(\text{OH})_3$ could take place at $\text{pH} > 4$, but we assume this to be negligible due to high ionic strength (activity coefficient $A(\text{Fe}^{3+}) = 0.01$) and slow kinetics.

Figure 3a shows the pH dependence of our calculated $\gamma(\text{HO}_2)$ for ammonium-sulfate aerosol at various Cu/Fe ratios. Aerosol pH is held fixed throughout each simulation. For a given Cu/Fe, $\gamma(\text{HO}_2)$ approaches unity with increasing pH, reflecting enhanced chemical loss of O_2^- and therefore reduced volatilization flux. This pH dependence of $\gamma(\text{HO}_2)$ is consistent with laboratory measurements. Mozurkewich et al. (1987) found higher $\gamma(\text{HO}_2)$ with neutral Cu-doped aerosols (LiNO_3) ($\gamma(\text{HO}_2) = 0.94$) than acidic Cu-doped aerosols (NH_4HSO_4) ($\gamma(\text{HO}_2) = 0.40$). At fixed pH, $\gamma(\text{HO}_2)$ increases with decreasing Cu/Fe ratio, resulting from the suppressed HO_2 production by (Reaction RA3) and enhanced HO_2 loss by $\text{Fe}(\text{III}) + \text{O}_2(-\text{I})$.

The TMI chemistry initiated by HO_2 uptake from the gas phase can lead to either production or loss of H_2O_2 (Fig. 1), and this can be expressed as a positive or negative H_2O_2 yield ($Y_{\text{H}_2\text{O}_2}$) associated with $\gamma(\text{HO}_2)$. Figure 3b shows the pH dependence of $Y_{\text{H}_2\text{O}_2}$ over a range of Cu/Fe ratios. $Y_{\text{H}_2\text{O}_2} = 0.5$ indicates that all HO_2 is converted to H_2O , $Y_{\text{H}_2\text{O}_2} = 0$ indi-

cates that all HO_2 is converted to H_2O , and $Y_{\text{H}_2\text{O}_2} < 0$ indicates a reactive uptake of H_2O_2 . When $\text{Cu/Fe} \leq 0.05$, $Y_{\text{H}_2\text{O}_2}$ decreases with increasing pH. This is in part due to the enhanced loss of aqueous HO_2 by (Reaction RA1) and $\text{Fe}(\text{III}) + \text{O}_2(-\text{I})$, resulting in suppressed production of H_2O_2 by (Reaction RA5). On the other hand, at higher pH, the oxidation of $\text{Fe}(\text{II})$ is enhanced by $\text{Fe}(\text{OH})^+ + \text{H}_2\text{O}_2$ which is five orders of magnitude faster than $\text{Fe}^{2+} + \text{H}_2\text{O}_2$. (Reaction RA6) and (Reaction RA7) then become the dominant sinks for $\text{Fe}(\text{II})$ and may lead to a reactive uptake of H_2O_2 ($Y_{\text{H}_2\text{O}_2} < 0$). The slight increase of $Y_{\text{H}_2\text{O}_2}$ at Cu/Fe = 0.1 while pH increases from 0 to 3 is mainly due to the enhanced H_2O_2 production by (Reaction RA2). This pathway becomes unimportant at lower Cu/Fe.

Figure 3c examines the sensitivity of $\gamma(\text{HO}_2)$ to a decrease of Cu concentrations from the 2.9×10^{-3} M assumed in the standard simulation, keeping a fixed Cu/Fe = 0.05. We find that the sensitivity is weak as long as Cu remains above 5×10^{-4} M (corresponding to a Cu solute mass fraction of 8.0×10^{-5}), consistent with the threshold value (mass fraction of $1\text{--}2 \times 10^{-4}$) for Cu-only chemistry noted in Thornton et al. (2008). For example, at $\text{pH} = 3$, $\gamma(\text{HO}_2)$ only decreases from 0.85 to 0.61 with a five-fold decrease of Cu concentrations. This weak response is mainly because uptake of HO_2 is limited by diffusion in the aqueous phase, reflecting its very fast reaction with Cu(II). As Cu(II) concentrations drop to values sufficiently low for HO_2 to become well-mixed into the aerosol, $\gamma(\text{HO}_2)$ then decreases rapidly with decreasing Cu. This dependence of $\gamma(\text{HO}_2)$ on Cu concentrations also appears to be consistent with laboratory measurements (Mozurkewich et al., 1987).

The aerosol budget can be significantly different in the presence of organic species in aerosols. First, TMI can readily form complexes with organic ions, such as oxalate, glyoxalate, and pyruvate (Moorhead and Sutin, 1966; Cooper and DeGraff, 1972; Zuo and Hoigné, 1994; Okochi and Brimblecombe, 2002; Deguillaume et al., 2005). While these organic complexes are in general less reactive towards $\text{HO}_2(\text{aq})$ and O_2^- than the free ions (Sedlak and Hoigné, 1993), TMI cycling can be greatly enhanced by the photoreduction and Fenton reaction of these organic complexes (Zuo and Hoigné, 1992; Sedlak and Hoigné, 1993). Second, these organic compounds are often highly concentrated in aqueous aerosols (Ervens and Volkamer, 2010; Ervens et al., 2011), leading to a significant loss of aqueous OH as well as enhanced gas uptake of OH (George et al., 2007; Abbatt et al., 2012). As a result, aqueous OH budget can be significantly affected by both OH sources and sinks. Furthermore, organic compounds can also provide a sink for $\text{HO}_2(\text{aq})$ and O_2^- (Bielski et al., 1983; Bielski et al., 1985). We do not consider this effect here for lack of adequate information.

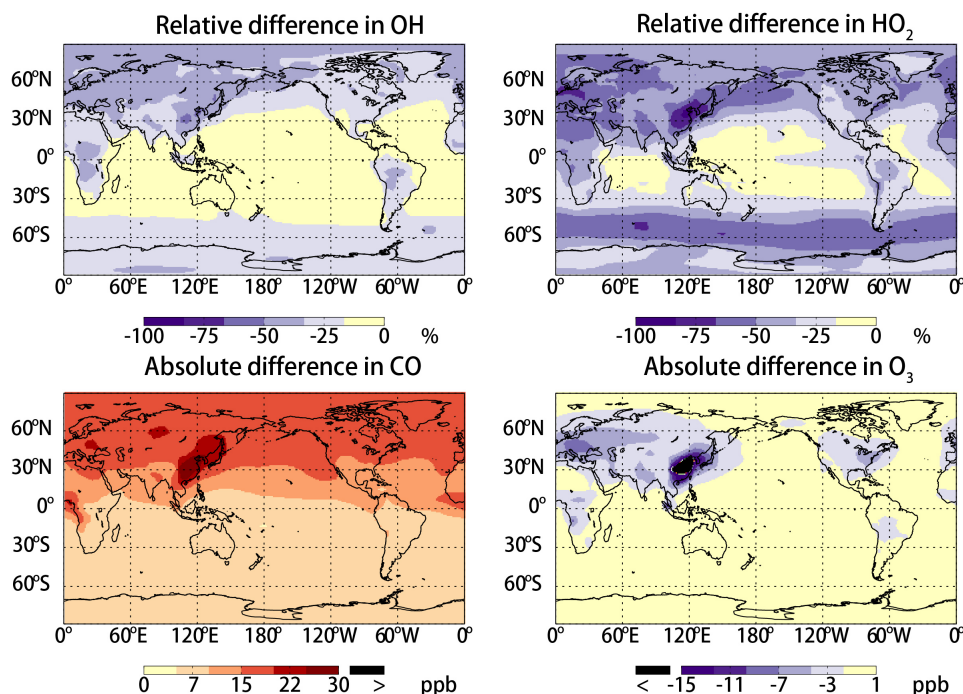


Fig. 4. Effect of HO_2 reactive uptake on non-cloud aerosols ($\gamma(\text{HO}_2) = 1$ producing H_2O) on surface air concentrations of OH, HO_2 , CO, and O_3 in the GEOS-Chem model. Values are annual means for 2005 and are calculated by difference with a simulation including no HO_2 uptake.

5 Global implications for atmospheric oxidant chemistry

We examine the potential global implications of Cu-Fe- HO_x cycling by incorporating the corresponding HO_2 uptake in the GEOS-Chem global model of aerosol-oxidant chemistry (v9-01-01, <http://www.geos-chem.org>). Values in Fig. 3a indicate $\gamma(\text{HO}_2)$ in the range 0.4–1 for typical rural aerosol Cu concentrations and Cu/Fe ratios at 298 K. At such high values, uptake of HO_2 can become diffusion-limited with little residual sensitivity to $\gamma(\text{HO}_2)$ (Fig. S1 in the Supplement). There are several reasons why such high $\gamma(\text{HO}_2)$ values might not be representative of the global troposphere. As shown in Fig. 3c, $\gamma(\text{HO}_2)$ becomes insignificant for $[\text{Cu}] < 1 \times 10^{-4} \text{ M}$, and the importance of such a threshold was previously noted by Thornton et al. (2008) for Cu-only chemistry. Cu concentrations could be much lower than assumed here in the remote troposphere and at high altitudes. There remain large uncertainties in the aerosol phase and mixing state. Also Cu and Fe may not be chemically available across aerosol types or size ranges due to their distribution, speciation and solubility (Furutani et al., 2011). On the other hand, the higher solubility of HO_2 at colder temperatures than the 298 K assumed here would increase $\gamma(\text{HO}_2)$ (Mao et al., 2010a). As pointed out in Table 1, field studies suggest the need for $\gamma(\text{HO}_2) \sim 1$ to explain HO_2 observations, and there is some evidence that H_2O_2 is not the product. Other mechanisms than the Cu-Fe- HO_x redox chemistry described

here could contribute to HO_2 conversion to H_2O in aqueous aerosols (Sect. 2 in the Supplement).

The standard GEOS-Chem model includes a parameterization of $\gamma(\text{HO}_2)$ taken from Thornton et al. (2008) for HO_2 uptake by pure water. The resulting $\gamma(\text{HO}_2)$ is typically less than 0.1 and the product is H_2O_2 , with no significant effects on global oxidant chemistry. Here we investigated the implications for oxidant chemistry of assuming as an upper limit $\gamma(\text{HO}_2) = 1$ for all aerosols. We further assume $Y_{\text{H}_2\text{O}_2} = 0$ (Fig. 3b), since observations suggest that the dissolved Cu/Fe ratio is usually below 0.1 (Table S4); in fact, it appears from Fig. 3b that $Y_{\text{H}_2\text{O}_2}$ is more likely to be negative than positive. Previous comparisons to aircraft and satellite observations suggest that GEOS-Chem provides a reasonable representation of aerosol loadings in the global troposphere (Drury et al., 2010; van Donkelaar et al., 2010; Fisher et al., 2011; Wang et al., 2011).

Figure 4 shows the difference of annual mean (2005) simulated surface air concentrations of OH, HO_2 , CO, and O_3 for the GEOS-Chem simulation with fast aerosol conversion of HO_2 to H_2O ($\gamma(\text{HO}_2) = 1$, $Y_{\text{H}_2\text{O}_2} = 0$) compared to a simulation with no HO_2 uptake. The effects are largest in the extratropical northern hemisphere and over the Southern Ocean, where aerosol loading is high and gas-phase photochemistry is slow. Surface OH and HO_2 concentrations decrease there by 20–30% and 40–60% respectively; the decrease in OH is partly compensated by an increase

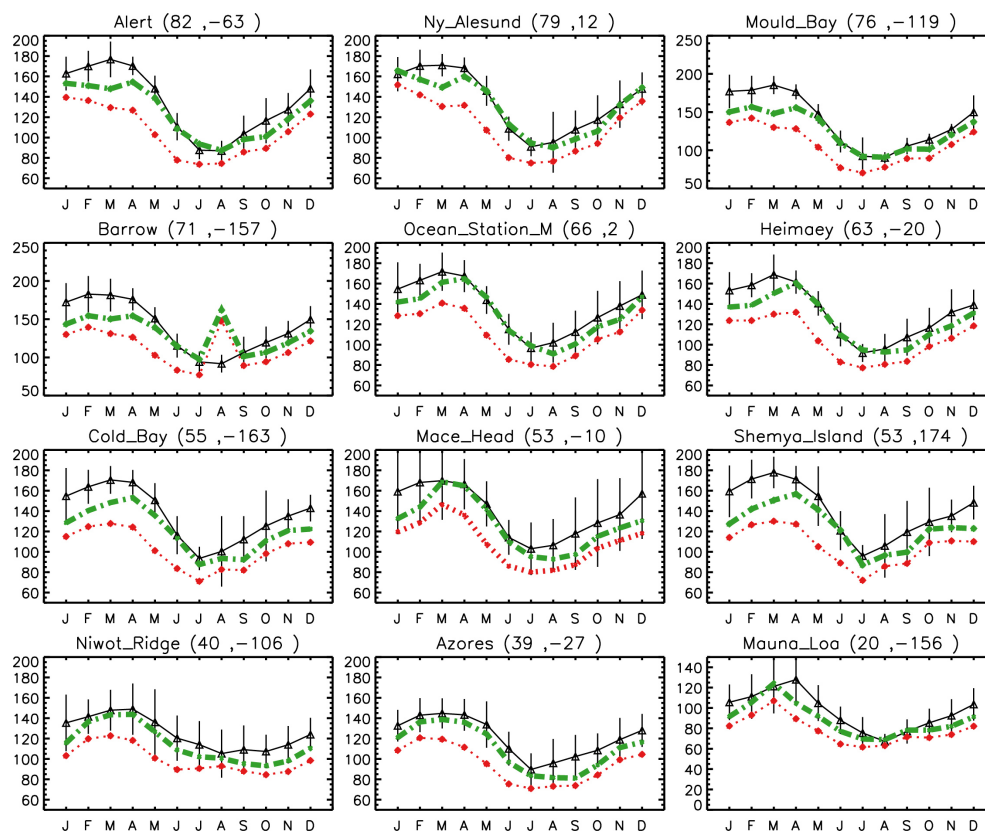


Fig. 5. Seasonal variation of CO concentrations at remote surface sites in northern extratropics. Climatological observations from NOAA/GMD (1988–2007) are shown in black. GEOS-Chem model values are shown in red with no HO₂ uptake and in green with $\gamma(\text{HO}_2) = 1$ producing H₂O.

in NO_x concentrations. The global mean (mass-weighted) tropospheric OH concentration in GEOS-Chem decreases by 12% from 12.4×10^5 to 11.0×10^5 molecules cm⁻³, improving agreement with observational constraints from methylchloroform ($10.8 \pm 0.8 \times 10^5$ molecules cm⁻³) (Prinn et al., 2005). The N/S interhemispheric OH ratio decreases from 1.09 to 1.02, in better agreement with the best estimate of 0.98 derived from the methylchloroform data (Krol and Lelieveld, 2003). The conversion of HO₂ to H₂O is critical for this effect. A sensitivity simulation with $\gamma(\text{HO}_2) = 1$ and $Y_{\text{H}_2\text{O}_2} = 0.5$ shows only a 3% decrease in global mean OH concentration.

The decrease of OH concentrations drives an annual mean increase of model CO concentrations by 20–30 ppb in the extratropical northern hemisphere, with maximum effect in spring. As shown in Fig. 5, this largely corrects the long-standing seasonal GEOS-Chem bias in that part of the world (Alvarado et al., 2010; Fisher et al., 2010; Kopacz et al., 2010). A similar CO bias in the extratropical northern hemisphere is found in other global models (Shindell et al., 2006) and may be similarly corrected.

Surface ozone concentrations decrease in general by 3–10 ppb over North America and Eurasia. Similar results over

North America were reported in a previous study (Horowitz et al., 1998). The largest decreases (up to 20 ppb) are in East Asia and help to correct model overestimates of surface ozone in that region (Wang et al., 2008). Comparison with surface ozone observations in the US from the Clean Air Status and Trends Network (CASTNet) shows a decrease of mean model bias from +7 to +3 ppb (Fig. S2). The production rate of global tropospheric ozone decreases from 5280 Tg yr⁻¹ to 4800 Tg yr⁻¹, and the loss rate decreases from 4660 Tg yr⁻¹ to 4240 Tg yr⁻¹. As a result, the change in global tropospheric ozone burden is rather small (about 1% decrease from 373 Tg to 369 Tg).

HO₂ conversion to H₂O in aqueous aerosols thus improves the simulation of tropospheric oxidant chemistry in GEOS-Chem and could improve other models as well. Anthropogenic aerosol concentrations are expected to decrease globally in the coming decades as a result of policies for improving air quality (Meinshausen et al., 2011). Our work suggests that this could have a detrimental effect on ozone air quality (Fig. 4) by decreasing HO_x radical scavenging. It could also lead to a previously unrecognized, indirect negative radiative forcing from aerosols by decreasing the lifetimes of the long-lived greenhouse gases methane and

hydrofluorocarbons (HFCs). The resulting negative radiative forcing from aerosol decrease would partly offset the positive radiative forcing from decreased aerosol and cloud scattering.

In summary, we have presented an aqueous chemical mechanism for rapid conversion of HO₂ to H₂O in aerosols, and have explored its potential impact on atmospheric chemistry. Although there are large uncertainties regarding the mechanism, there is evidence from field observations that this rapid conversion does take place, and implementing it in GEOS-Chem shows large effects. A better understanding of aqueous HO₂ chemistry in atmospheric aerosols requires substantial work in many aspects. Measurements of aerosol Cu and Fe speciation would be of particular value as speciation could greatly affect the kinetics. More information is needed for the remote troposphere on Cu and Fe concentrations, solubility, and internal mixing across aerosol types. Redox coupling involving other TMI present in atmospheric aerosols (Heal et al., 2005) should be investigated (Marcus, 1993). Better characterization of aqueous-phase kinetics is needed including reaction rate constants and complexation equilibria with ionic strength and temperature dependences. Furthermore, organic compounds have been found to be abundant in aerosols (Ervens and Volkamer, 2010). Oxidation of organic species provides a sink for OH in aerosols, while photoreduction and Fenton reaction of organic complexes could provide a source. In future studies, the aqueous chemical mechanism could be improved by including organic compounds and halogen species, such as in CAPRAM (Ervens et al., 2003).

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/13/509/2013/acp-13-509-2013-supplement.pdf>.

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